The Reaction Chemistry of Aluminum(I, III) Compounds Stabilized by Sterically Bulky Ligands

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Dedicated to my wife Qiaozhu Jiang

and my son Yicheng Zhu

for their love and affection

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The Reaction Chemistry of Aluminum(I, III) Compounds Stabilized by Sterically Bulky Ligands

1. Introduction

Aluminum, bound almost exclusively to oxygen in various combinations, is the most abundant metal in the earth's crust. Once methods were developed to free useable quantities of the element from oxygen, applications for the element began developing rapidly. This growth has resulted in the ubiquity of the metal in today's world.[1]

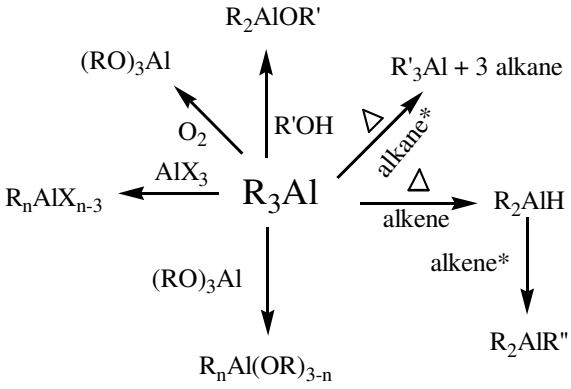
The organoaluminum chemistry, due to the implications and potential, has been significant enough to excite widespread industrial interest. In 1859, ethylaluminum sesquiiodide (a 1:1 mixture of $EtAlI_2$ and Et_2AlI) was first prepared from ethyl iodide and aluminum by Hallwachs and Schafarik.[2] The subsequent synthesis of aluminum alkyls from mercury alkyls and aluminum metal was reported by Buckton and Odling in 1865.[3] The development of organoaluminum chemistry including the introductions of many new synthetic methods followed by researches on organomagnesium and organolithium reagents, the syntheses of a large number of new organoaluminum compounds, and the explorations of reactions of these compounds, however, started from the studies of Ziegler et al. in the early 1950's. These studies open a wide insight into the organoaluminum chemistry which lies dormant for ca. one hundred years, and make the potential of organoaluminum reagents for organic synthesis and polymerization come to light. The most notable important discovery is the polymerization of ethylene by Ziegler through a stepwise addition to triethylaluminum.[4,5] This directly leads to the generation of Ziegler's catalysts based on transition-element compounds, which are normally formed by reaction of a transition-element halide or alkoxide or alkyl or aryl derivative with aluminum alkyl or alkyl halide.[6] Correspondingly, the reactivity of the related organoaluminum compounds (Scheme 1) can be presented as follows:[7]

a) The highest reactivity is observed if all three valences of Al are bound to C or C and H, respectively.
b) Many reactions are related to the electron deficiency of aluminum in its compounds of the type $AlR_{3-n}X_n$ (n = 2 to 0).

c) Certain reversible relations exist between the Al–C and the Al–H bond.

d) Not only the Al–H group but also Al–C moiety can be added to C=C and C≡C bonds.

e) Organoaluminum compounds undergo a series of reactions more or less characteristic for many metal alkyls in which the aluminum is removed from carbon.



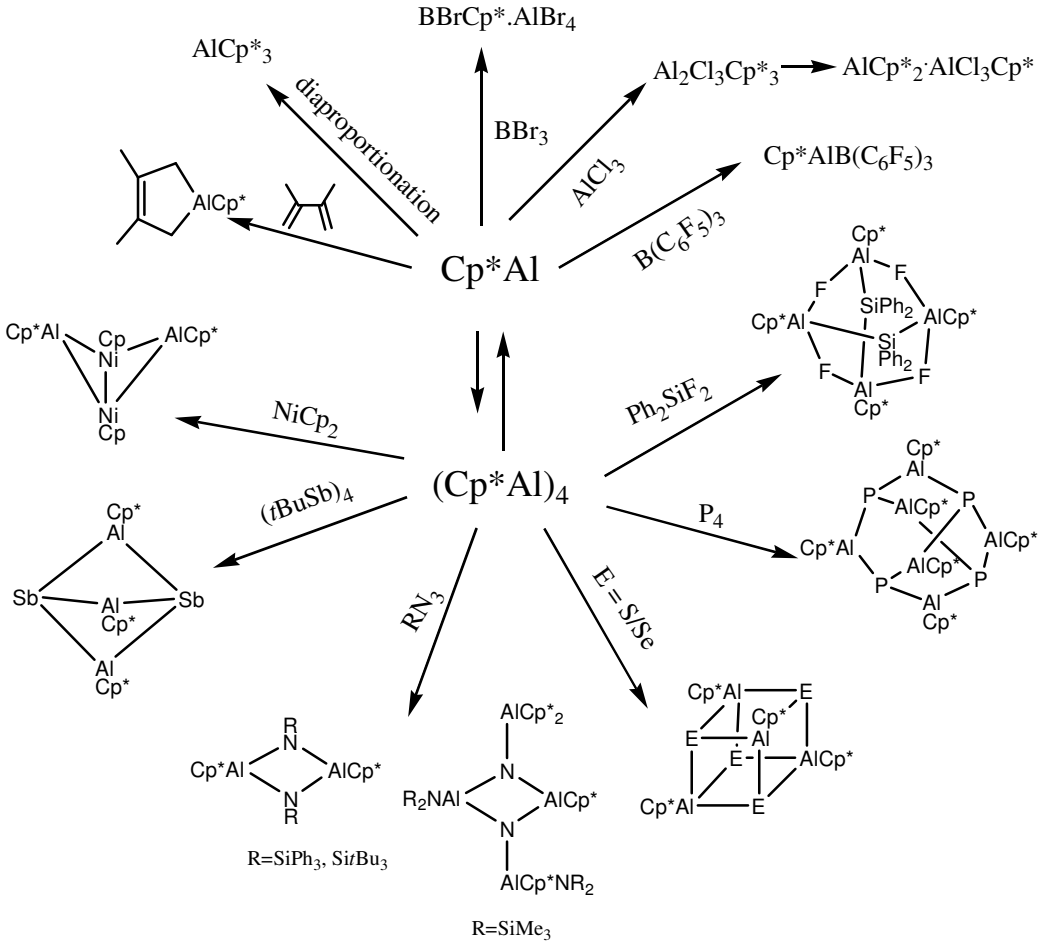
Scheme 1

In the following time, the organoaluminum chemistry was rapidly developed on the basis of Ziegler's classic studies, and some new properties of organoaluminum compounds are found. For example, alumoxanes prepared from the controlled hydrolysis of organoaluminum compounds or alternatively by their reactions with oxygen-containing compounds can be used as active catalysts in the polymerization of epoxides, aldehydes, and olefins.[8-14] In 1980, methylalumoxane (MAO) was found to be a highly active cocatalyst for group 4 metallocenes catalyzing ethylene and propylene polymerization by Kaminsky and Sinn.[15-16] This has been of remarkable industrial importance.

In the meantime, the reactions of organoaluminum compounds towards unsaturated substrates, elements, or acidic hydrogen containing species are studied more systematically, comprehensively, and in detail, and many reaction types such as elimination, addition, insertion, reoxidation, C–H activation, dimerization (or oligomerization), and substitution are presented.[4]

In comparison to the trivalent organoaluminum chemistry, the low valent aluminum(I, II) chemistry which is characterized by the restricted use of the valence electrons of Al in

compound formation is often invoked due to the roles of these Al(I, II) species as possible intermediates in photochemical and radical reactions. Although the pursuit of compounds of low valent aluminum has a long history of over 50 years, most of the fascinating progress occurs only in recent years, especially in the case of Al(I) which may prove to be of much importance in the near future (Scheme 2).[17-18]

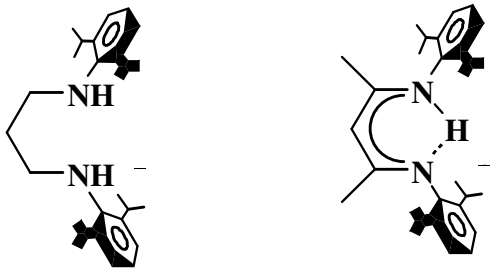


Scheme 2

In view of the syntheses of organoaluminum compounds, some of formula AlR_nX_{3-n} (n = 1-3) with simple R groups (R = H, Me, Et, *i*Pr, *t*Bu) have been commonly employed as hydroalumination or carboalumination reagents. These compounds have been commercially available. Due to the strong Lewis acidity of the Al center in these compounds, their reaction products are often found in high degree of association, even for reagents with fairly large organic groups such as *t*Bu, Ph. A large number of clusters of alane or carboalane with two- or three-dimensional net or cage structures have been synthezied, exhibiting the extensive

organoaluminum chemistry. However, studies of this aspect often meet with challenges in detailed investigations of mechanism and stoichiometry.

The bulky organic ligand is usually employed to stabilize the metal center electronically and/or sterically. The introduction of a bulky organic ligand whether as a simple Lewis base donor, or in elimination reactions by gas (H_2, RH) or MX_n salts to the Al center, in fact, can efficiently reduce the condensation of products, and meanwhile, result in the formation of unusual compounds. This has also been successfully applied for the synthesis of low valent aluminum compounds. Moreover, by the stabilization of these large ligands, we can selectively perform changes of the functionalities at Al, and intendedly control and design the reaction. All these help to understand organoaluminum chemistry and to investigate the possible reaction mechanisms.



L'H$_2$ **LH**

Scheme 3

In this thesis, the two types of bulky ligands (Scheme 3) are employed for the synthesis of aluminum monohydride, monohalide, and monoalkyl (using L'H_2), and aluminum(I) monomer, aluminum(III) dihydride and dihalide, and aluminacyclopropene (using LH), respectively. Subsequently, these compounds are further used as precursor to react with Lewis acidic species, fluorination agent, oxidation agents, carbene, water, unsaturated molecules, and so on. The sections 2.1.-2.8. will in detail point out the importance, recent research background, experimental results and discussion, and conclusion and remark of the chemistry

of the bulky ligands stabilized aluminum compounds and their reactions. Based on these delineations, the objectives of the present work are:

(1) the chemical changes of aluminum functionalities in the stabilization of bulky ligands at Al.

(2) the exploration of the reaction chemistry of the aluminum(I) monomer LAl.

(3) the exploration of reaction chemistry of aluminacyclopropene LAl(η^2-C_2RR').

2. Contents

2.1. A Bulky Chelating Diamide Aluminum Monohydride: Synthesis, Structure, and Reactions with Me_3SnF and Heavy Group 16 Elements

*Abstract: A bulky chelating diamide aluminum monohydride [ArN(CH$_2$)$_3$NAr]AlH(NMe$_3$) (Ar = 2,6-iPr$_2$C$_6$H$_3$) (**1**) was prepared in excellent yield from the reaction of diamine ArNH(CH$_2$)$_3$HNAr with a small excess of AlH$_3$·NMe$_3$ in toluene. Subsequent fluorination of **1** with Me$_3$SnF resulted in the formation of an aluminum monofluoride [ArN(CH$_2$)$_3$NAr]AlF(NMe$_3$) (**2**), indicating the reactivity of **1** despite the bulk of diamido ArN(CH$_2$)$_3$NAr. Further reaction of **1** with elemental E (E = S, Se and Te) proceeded in toluene at elevated temperature to yield aluminum chalcogenide {[ArNH(CH$_2$)$_3$NAr]Al(μ-E)}$_2$ (E = S (**3**), Se (**4**), and Te (**5**)). Compounds **1** and **2** are well-separated monomers with a central aluminum atom in a tetrahedral environment. Compound **4**, however, is a dimer with a central Al$_2$Se$_2$ core bearing an ideal four-membered planar ring. The IR and ^{1}H NMR spectral data of compounds **3**–**5** suggest that a migration of the hydrogen from selenium to one of the nitrogen atoms at the diamide ligand is involved in the course of the reaction.*

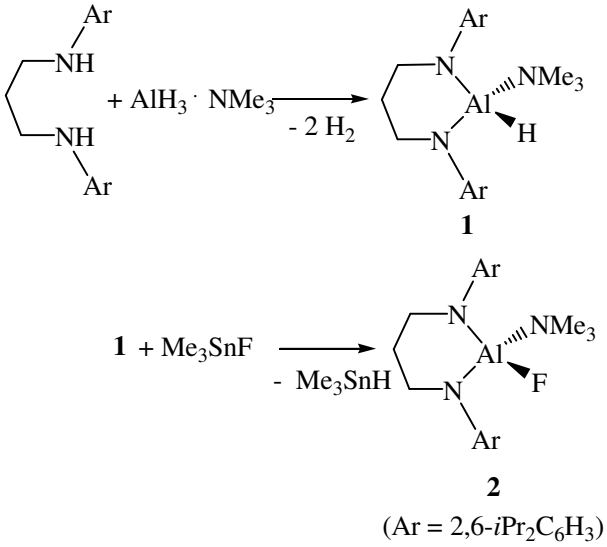
Studies of aluminum hydrides have received considerable attention due to their scientific importance and numerous applications.[4] In recent years, much work has been devoted to aluminum hydrides in low aggregation, especially to the monomeric forms, since the synthetic process of monomeric aluminum hydride helps us to understand the reaction chemistry of surface-bound AlH_n groups developed during thin film growth from organoaluminum sources.[19-20] Moreover, aluminum hydrides of low aggregation can be used as very effective precursors for preparing aluminum chalcogenides.[21] However, reactions involving aluminum hydrides of low aggregation with chalcogen or organochalcogenides have been reported to a lesser extent. Raston et al.[22-25] investigated the reaction of trimethylamine adduct of alane

$Me_3N{\cdot}AlH_3$ with chalcogen or organochalcogenide. Power et al.[26] reported one example of the reaction of aluminum dihydride with organochalcogenide and our group discussed the reaction of a series of aluminum dihydrides with chalcogen,[21,27-30] where the isolation and structural characterization of some novel compounds (such as $LAl(SeH)_2$, LAl(SeH)Se(SeH)AlL,[21] $LAl(SH)_2$[27] (L = N(Ar)C(Me)CHC(Me)N(Ar), Ar = 2,6-*i*$Pr_2C_6H_3$); $(RAlE)_2$ (R = 2,4,6-*t*$Bu_3C_6H_2$, E = S;[26] R = $N(SiMe_3)C(Ph)C(SiMe_3)_2$,[28] 2,6-$(Et_2NCH_2)_2C_6H_3$, 2-$Et_2NCH_2$-6-$MeC_6H_3$,[29] E = Se, Te), *trans*-[$\{Me_3N(H)Al(\mu\text{-}E)\}_2$] (E = Se, Te),[23] *trans*-[$\{Me_3N(PhTe)Al(\mu\text{-}Se)\}_2$];[24] [($\eta^1$-3,5-*t*$Bu_2$pz($\mu$-Al)H]$_2$E (E = S, Se, Te);[30] $Me_3NAl(ER)_3$ (E = Se, R = Et, Ph, CH_2Ph; E = Te, R = Ph)[22] and $Al_4Se_5(H)_2(NMe_3)_4$[24]) showed a rich chemistry. Nonetheless, the reaction of monomeric bulky aluminum monohydrides with chalcogen, which might generate the corresponding monomeric Al–EH moieties, have not been reported so far. Therefore we became interested in finding the sufficiently bulky ligand to synthesize the intramolecularly stabilized aluminum monohydride, and further studies on its reactivity.

The divalent bulky chelating diamide ligand $[ArN(CH_2)_3NAr]^{2-}$ (Ar = 2,6-*i*$Pr_2C_6H_3$) is currently exhibiting growing interests[31] due to its special steric and electronic properties to control effectively the geometry at the metal center. The known complexes having this ligand include main group metal (Li, K, Al) and transition metal (Ti, Zr, Y, Lu) derivatives.[31-35] The only reported aluminum complexes are a series of compounds containing alkyl and aryl groups $[ArN(CH_2)_3NAr]AlR$ (R = Me, *i*Bu, C_6F_5).[35] Herein we report on the synthesis and characterization of a bulky chelating diamide aluminum monohydride $[ArN(CH_2)_3NAr]AlH(NMe_3)$ (Ar = 2,6-*i*$Pr_2C_6H_3$) (**1**). The metathesis of **1** with Me_3SnF to give a monofluoride $[ArN(CH_2)_3NAr]AlF(NMe_3)$ (**2**) and its reaction with heavy group 16 elements to afford dimeric aluminum chalcogenide $\{[ArNH(CH_2)_3NAr]Al(\mu\text{-}E)\}_2$ (E = S (**3**), Se (**4**), and Te (**5**)) are also described.

Although the syntheses of aluminum hydrides have been reported in a number of publica

-tions,[36] the use of $AlH_3{\cdot}NMe_3$ as a precursor to react with *N*-substituted diamine, diimine and analogues containing NH groups or $E(SiMe_3)_2$ (E = P, As) under elimination of H_2 or $HSiMe_3$ has shown a facile route to aluminum hydrides of low aggregation.[21,37-44] Reaction of the diamine $[ArNH(CH_2)_3HNAr]$ with a small excess of $AlH_3{\cdot}NMe_3$ in toluene under heating (80 ˚C) affords the intramolecularly stabilized diamide aluminum monohydride $[ArN(CH_2)_3NAr]AlH(NMe_3)$ (**1**) in excellent yield. Subsequent fluorination of **1** with Me_3SnF either at room temperature or at elevated temperature (80 ºC) results in the formation of an aluminum monofluoride $[ArN(CH_2)_3NAr]AlF(NMe_3)$ (**2**, Scheme 4).



Scheme 4

Complexes **1** and **2** are characterized by NMR, MS (EI), IR spectroscopy and elemental analyses. The presence of hydride in **1** is evident from the IR spectrum. The broad IR band at 1799 cm^{-1} can be assigned to the Al–H stretching absorption.[45] In the IR spectrum of **2**, this absorption disappears, indicating a complete fluorination of **1**. The ^{19}F NMR spectrum of **2** exhibits one singlet resonance (–175.4 ppm), which can be comparable to those terminal Al–F resonances in a series of compounds $(ArN[Si(R)Me_2]AlF_2{\cdot}THF$: Ar = 2,6-$iPr_2C_6H_3$, R = Me, –178.1; R = *i*Pr, –177.0; R = *t*Bu, –175.1; Ar = 2,6-$Me_2C_6H_3$, R = *t*Bu, –175.0; R = 2,4,6-$Me_3C_6H_2$, –175.9 ppm).[46] In the ^1H NMR spectra of **1** and **2** the presence of the complex resonances for the backbone protons of the diamide ligand (two isopropyl methine ($CHMe_2$),

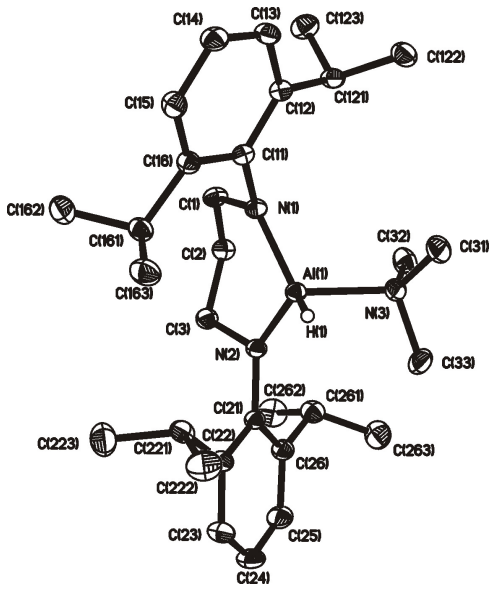


Figure 1. Molecular structure of **1**. H atoms are omitted for clarity except for the Al–H group. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.820(1), Al(1)–N(2) 1.828(1), Al(1)–N(3) 2.024(2), Al(1)–H(1) 1.52, N(1)–Al(1)–N(2) 106.52(6), H(1)–Al(1)–N(3) 96.0.

four isopropyl methyl ($CHMe_2$), two methene (NCH_2) and two methene (NCH_2CH_2) resonances) are consistent with a pseudotetrahedral geometry and *Cs* symmetry about Al. Similar resonances are observed in compounds [M{$ArN(CH_2)_3NAr$}(η-C_5H_5)Cl] (M = Zr, Y; Ar = 2,6-iPr$_2$C$_6$H$_3$).[31,33] The resonance for the Al–H proton in **1** is not seen, which is, however, typical for amidoaluminum hydride species.[38] Substitution of Al–H in **1** by Al–F has a stronger effect on the chemical shift of the NMe_3 group (1.66, **1**; 1.75 ppm, **2**), while a smaller effect is observed for the backbone protons of the ligand. The MS (EI) spectrum shows the molecular ion of [$M^+ - NMe_3$] for **1**, and [M^+] and [$M^+ - NMe_3$] for **2** and the single crystal X-ray structural determinations of **1** and **2** confirm the composition of [$ArN(CH_2)_3NAr$]$AlR(NMe_3)$ (R = H, **1**; F, **2**), where the former contains half a molecule of *n*-hexane per molecule of complex **1** in the asymmetric unit.

Compounds **1** and **2** are well-separated monomers with a central aluminum atom both in a distorted tetrahedral environment (Figures 1 and 2 with selected bond lengths and angles). The terminal Al–H bond length (1.52 Å) is closer to those in compounds (2,4,6-tBu$_3$C$_6$H$_2$)$_2$AlH[47] (1.53(4) Å) and [$HAl(NMe_2)_3$]$^-$[48] (1.52(2) Å), but shorter than those in

AlH(Cl)[*t*BuNCH$_2$CH$_2$N(*t*Bu)H][37] (1.60 Å), Al$_2$(μ-NEt$_2$)$_2$[N(*i*Pr)$_2$]$_2$H$_2$[49] (1.67 Å) and (2,4,6-*t*Bu$_3$C$_6$H$_2$)Al(H)Cl·THF[50] (1.73(5) Å). The terminal Al–F separation (1.678(1) Å) is in the range of 1.657–1.681 Å observed in compound [(Me$_3$Si)$_3$CAlF$_2$]$_3$[51] and somewhat longer

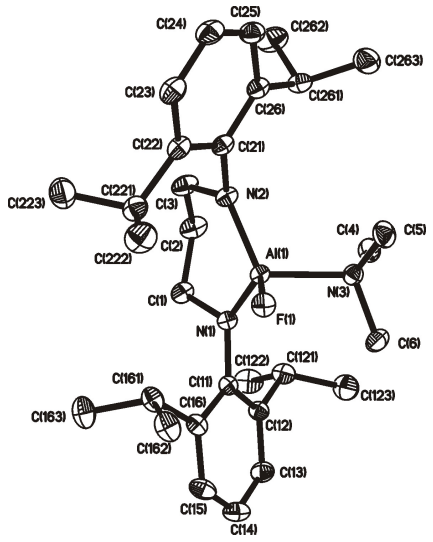


Figure 2. Molecular structure of **2**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Al(1)–N(1) 1.810(2), Al(1)–N(2) 1.804(2), Al(1)–N(3) 2.000(2), Al(1)–F(1) 1.678(1), N(1)–Al(1)–N(2) 107.45(7), F(1)–Al(1)–N(3) 93.00(6).

than those in [{(2,6-*i*Pr$_2$C$_6$H$_3$)N(SiMe$_3$)AlF$_2$}$_3$][46] (1.634–1.642 Å) and AlF$_3$[52] (1.63 Å), as determined by electron diffraction. The diamide ligand chelates the Al atom to form an AlN$_2$C$_3$ six-membered non-planar ring, in which Al(1) and C(2) occupy the head positions with distances to the quasi-plane N(1)–N(2)–C(3)–C(1) (the mean deviation Δ = 0.0716 Å) of 0.1034 and 0.6852 Å in **1** and the plane N(1)–N(2)–C(3)–C(1) (Δ = 0.0316 Å) of –0.0109 and 0.6730 Å in **2**, respectively. It is obvious that the former displays a boat conformation and the latter a flattened chair conformation, as can be explained in terms of strain imposed by the Ar group. The F atom owns a stronger electron attractive tendency than the H atom. This generates different charge distribution for the central Al atom of **1** and **2**, and gives rise to a small difference of the Al–N$_{diamide}$ bond distance between **1** and **2** (average 1.824, **1**; 1.807 Å, **2**), as well as the Al–N$_{NMe3}$ bond distance (2.024(2), **1**; 2.000(2) Å, **2**) and the N(1)–Al(1)–N(2) chelating angle (106.52(6), **1**; 107.45(7)°, **2**). The Al–N$_{diamide}$ distances in **1** and **2** can be

compared with the terminal Al–N (amide) distances in $CH_2(CH_2CMe_2)_2NAlH_2{\cdot}NMe_3$[44] (1.838(2) Å), AlH(Cl)[*t*BuNCH$_2$CH$_2$N(*t*Bu)H][37] (1.80(1) Å) and {Al(μ-H)[N(CMe$_2$CH$_2$)$_2$CH$_2$]$_2$}$_2$[53] (1.836(3) Å), and are longer than the Al–$N_{diamide}$ bond lengths in the three coordinate aluminum compound [ArN(CH$_2$)$_3$NAr]AlMe[35] (1.760(3), 1.766(3) Å). The Al–N_{NMe3} distances in **1** and **2** are as expected in a comparable range.[44,54-55]

The successful fluorination of **1** using Me_3SnF is indicative of its reactivity despite the steric hindrance of the bulky ligand. Treatment of **1** with equivalent amounts of sulfur, selenium and tellurium proceeded in toluene at elevated temperature to afford solvated aluminum sulfide (**3**) as light yellow crystals, selenide (**4**) as yellow crystals and telluride (**5**) as green-yellow crystals, respectively. The former two compounds are obtained in good yield and the latter in moderate yield (Equation 1).

$$2[ArN(CH_2)_3NAr]AlH(NMe_3) + 2E \rightarrow \{[ArNH(CH_2)_3NAr]Al(\mu\text{-}E)\}_2 + 2NMe_3 \quad (1)$$

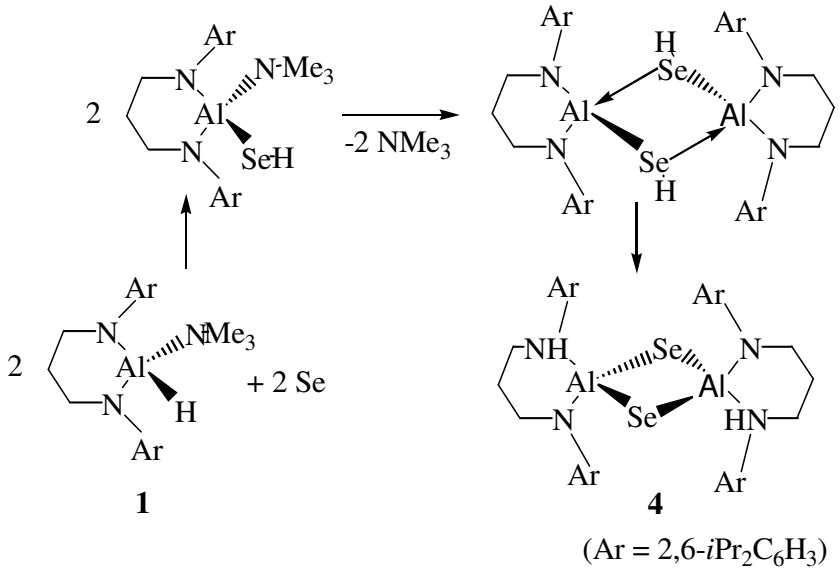
E = S (**3**), 80 ºC, 12 h

= Se (**4**), reflux, 12 h

= Te (**5**), reflux, 120 h

Compounds **3**–**5** are air and moisture sensitive and soluble in hot toluene and benzene, while poorly soluble in THF, $CHCl_3$ and *n*-hexane. They were characterized by IR and NMR spectroscopy and MS (EI) spectrometry, as well as elemental analyses. The MS (EI) spectra of **3**–**5** show the dimeric molecular ion with the correct isotope pattern and their ^{1}H NMR spectroscopies show the very similar characters of the ligand including the resonances of solvent toluene protons. The doublets in the range of δ 1.10–1.25, one septet centered at ca. δ 3.38 and a multiplet at δ 7.02–7.10 are corresponding to the protons of the 2,6-*i*Pr$_2$C$_6$H$_3$ group. One broad singlet at ca. δ 1.36 can be assigned to NH resonance[37,39] with satisfied integral intensity indicating two protons. Two areas of unresolved multiplet resonances centered at ca. δ 1.78 and 3.00 arise from the six non-equivalent methylene protons, where the latter might be formed from overlapping proton resonances of the two amido NC*H*$_2$ and two

amine HNCH_2 groups. The IR spectra exhibit the NH absorption in the $\tilde{\nu}_{NH}$ region[37-38] (3190, **3**; 3187, **4**; 3185 cm^{-1}, **5**). All these data indicate that compounds **3**, **4** and **5** have the same structure corresponding to the formula of $\{[ArNH(CH_2)_3NAr]Al(\mu\text{-}E)\}_2$.



(Ar = 2,6-*i*$Pr_2C_6H_3$)

Scheme 5

The reaction of aluminum dihydride with selenium has been discussed in our group,[21,28-29] where the formation of a dimeric compound might proceed through an Al–SeH intermediate. In a similar way the reaction of aluminum monohydride **1** with selenium might involve the formation of intermediate $[ArN(CH_2)_3NAr]Al(SeH)(NMe_3)$, which dimerizes to produce $\{[ArN(CH_2)_3NAr]Al(\mu\text{-}SeH)\}_2$ under elimination of gaseous NMe_3. However, with reference to related Al–SeH compounds $LAl(SeH)_2$ and LAl(SeH)Se(SeH)AlL (L = N(Ar)C(Me)CHC(Me)N(Ar), Ar = 2,6-*i*$Pr_2C_6H_3$),[56] no absorptions in the range of 2000-2500 cm^{-1} in the IR spectrum are observed to indicate the formation of an Al–SeH moiety. This suggests that the dimer $\{[ArN(CH_2)_3NAr]Al(\mu\text{-}SeH)\}_2$ is not stable under heating and the hydrogen atom attached to selenium atom migrates quickly to one of the nitrogen atoms at the diamide ligand to afford stable compound **4**. The most likely mechanism is given in Scheme 5. The formation of compounds **3** and **5** might be similar to that of **4**.

A suitable single crystal of compound **4** was measured by X-ray diffraction. The structure analysis of compound **4** shows a dimeric species containing two molecules of toluene.

Unfortunately, the quality of the crystal structure did not allow the location of the hydrogen atoms on the nitrogen atoms. Nevertheless, the presence of NH groups was established by IR and ^{1}H NMR spectroscopy. The molecular structure is viewed in Figure 3 with selected bond lengths and angles. The Al(1)–N(1) (1.932(11) Å) and Al(1)–N(2) (1.916(11) Å) bond distances are midway between the Al–N_{amine} and Al–N_{amido} bond distances observed in complex AlH(Cl)[*t*BuNCH$_2$CH$_2$N(*t*Bu)H][37] (Al–N(1) (amine) (2.00(1) Å and Al–N(2) (amid

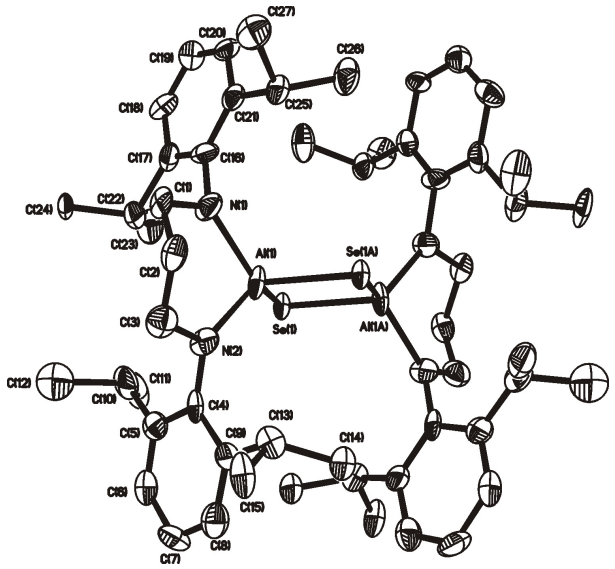


Figure 3. Molecular structure of **4**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Al(1)–N(1) 1.932(11), Al(1)–N(2) 1.916(11), Al(1)–Se(1) 2.339(1), Al(1)–Se(1A) 2.381(1), N(1)–Al(1)–N(2) 98.13(14), Se(1)–Al(1)–Se(1A) 101.44(5).

-o) (1.80(1) Å), and are longer than those Al–N distances found in compound Al[*t*BuNCH$_2$CH$_2$N(*t*Bu)][*t*BuNCH$_2$CH$_2$NH(*t*Bu)][38] in which the unique amine nitrogen center is disordered over all four nitrogen centers (1.850(5), 1.870(5) Å), and much longer than Al–N_{amido} distances in **1** (1.820(1), 1.828(1) Å) and **2** (1.804(2), 1.810(2) Å). However, compared to compound AlH(Cl)[*t*BuNCH$_2$CH$_2$N(*t*Bu)H],[37] where the remarkable difference (0.20 Å) between Al–N(1) (amine) and Al–N(2) (amido) was observed, the very slight difference (0.016 Å) between Al(1)–N(1) and Al(1)–N(2) in **4** may imply the disorder of the two hydrogen atoms over the sides of all four nitrogen centers. Moreover, the similar

coordinated environments and approximately planar co-ordination geometries at the N(1) and N(2) (at N(1), Al(1)–N(1)–C(1) 119.6(8)°, Al(1)–N(1)–C(16) 126.4(8)°, C(1)–N(1)–C(16) 113.2(9)°, ∑(C–N–Al, C) = 359.2°; at N(2), Al(1)–N(2)–C(3) 121.1(9)°, Al(1)–N(2)–C(4) 130.1(7)°, C(3)–N(2)–C(4) 108.0(9)°, ∑(C–N–Al, C) = 359.2°) do not allow to distinguish between the amine nitrogen and the amido nitrogen centers. Overall, it is assumed that the almost equal possibility of the hydrogen migration from the selenium atom to any nitrogen atom at the diamide ligand is included in the course of the reaction.

The Al_2Se_2 core exhibits an ideal planar ring (the least-square deviation Δ = 0.0005) with Al(1)–Se(1) of 2.339(1) Å, Al(1)–Se(1A) of 2.381(1) Å and Al(1)–Se(1)–Al(1A) of 78.56(5)º, which are as expected in a range for Al_2Se_2 core compounds,[22-23,28-29] while the Al(1)–Se(1) and Al(1)–Se(1A) distances differ by ca. 0.042 Å probably due to steric effects of the backbone ligand toward the Al_2Se_2 ring. The ligand chelates the Al atom to fuse two six-membered AlN_2C_3 rings, which are arranged *in trans* on each side of Al_2Se_2 core. The two AlN_2C_3 rings both display a boat conformation with Al(1) and Al(1A) at the bow and C(2) and C(2A) at the stern, respectively, and are almost arranged perpendicularly to the Al_2Se_2 ring (the dihedral angle between the ring (Al_2Se_2) and the plane (N(1)–N(2)–C(3)–C(1), Δ = 0.0238 Å) is 90.5º).

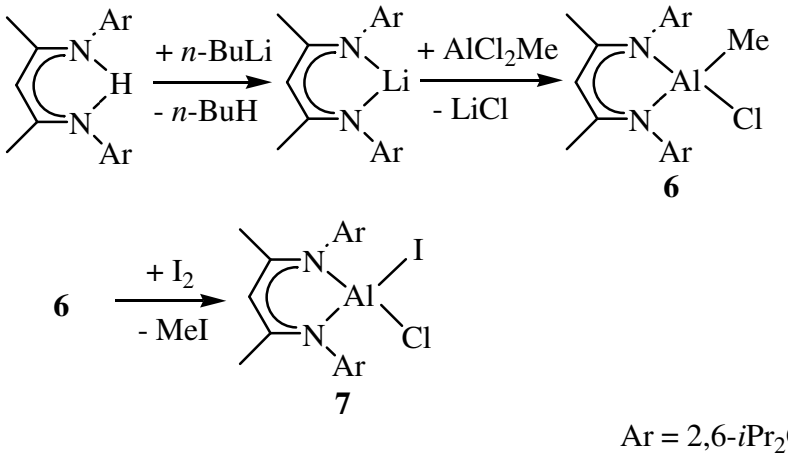
Thus, it has been shown that the $[ArN(CH_2)_3NAr]^{2-}$ ligand forms a stable chelate with the aluminum hydride. The hydride functionally can be replaced by a fluorine atom or substituted by a chalcogen (S, Se, Te) under migration of the hydrogen to an adjacent nitrogen of the chelating ring. The latter reaction does not yield an aluminum chalcogen double bond system but rather a four-membered ring of composition Al_2E_2 (E = S, Se, Te).

2.2. The Stepwise Hydrolysis of Aluminum Chloride Iodide LAlClI in the Presence of *N*-Heterocyclic Carbene as Hydrogen Halide Acceptor

*Abstract: An aluminum chloride iodide LAlClI (**7**, L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-i$Pr_2C_6H_3$) has been synthesized to study the stepwise hydrolysis of this compound in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene as hydrogen halide acceptor. The isolation and characterization of the aluminum chloride hydroxide [LAlCl(μ-OH)]$_2$ (**8**) and the dihydroxide LAl(OH)$_2$ (**9**) demonstrate the realization of a controlled hydrolysis.*

The controlled hydrolysis of organoaluminum compounds is of great interest since it can lead to the formation of alumoxanes which are used as active catalysts and cocatalysts for the polymerization of a wide range of organic monomers.[8-16,57-59] Furthermore, it can be useful to generate organoaluminum hydroxides, oxides, or oxide hydroxides.[12,57-58,60-65] On one hand, the reaction of AlR_3 compounds (R = Me, *t*Bu, Mes, or Ph)[66-67] with water or hydrated inert salts afforded some aggregated alumoxanes $[RAlO]_n$, aluminum hydroxides, and oxide hydroxides. On the other hand, it has been shown that aluminum hydrides,[71-72] alkyls,[73] or aluminum amino-amides[74] stabilized by bulky organic ligands can be used as precursor for the synthesis of organoalumoxanes, organoalumoxane hydrides, and hydroxides by employing H_2O, or water-containing compounds (for example, $H_2O{\cdot}B(C_6F_5)_3$). In most cases the bulky ligand at the aluminum center hinders the aggregation of the hydrolysis products. However it has an effect on the stabilization of the metal whether electronically or sterically, and can result in the formation of unusual complexes, such as L'Al=O·$B(C_6F_5)_3$ (L' = $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$).[73] More recently, we have reported the reaction of $LAlI_2$ (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$) with KOH containing a small amount of H_2O and KH in a liquid ammonia/toluene two-phase system and successfully isolated the first terminal aluminum dihydroxide $LAl(OH)_2$ supported by the bulky L ligand.[75] An improved route to $LAl(OH)_2$ was realized by using a strong nucleophilic

reagent, *N*-heterocyclic carbene as a HCl acceptor for the reaction of $LAlCl_2$ and stoichiometric amounts of water.[76] In the course of the synthesis of $LAl(OH)_2$ from $LAl(Hal)_2$ (Hal = I, Cl), a stepwise process was proposed.[75] However, there was no experimental evidence for the formation of LAl(OH)Cl or LAl(OH)I as an intermediate. In this context we report on the preparation of aluminum chloride iodide LAlClI (**7**) and its stepwise reaction with water by using a *N*-heterocyclic carbene as hydrogen halide acceptor, as well as isolation of the intermediate $[LAlCl(\mu\text{-}OH)]_2$ (**8**).



Scheme 6

The toluene/*n*-hexane solution of LLi prepared from LH and *n*-BuLi was directly used for the reaction with $AlCl_2Me$. Compound LAlClMe (**6**) was obtained as crystalline solid, its composition was confirmed by EI-mass and ^1H NMR measurements as well as by elemental analysis. The reaction of **6** with one equiv of I_2 within 5 days at room temperature resulted in the formation of compound LAlClI (**7**) as very light yellow crystals (Scheme 6). Compound **7** melts at 200–203 °C and the EI-mass spectrum indicates its monomeric nature in the gas phase (*m/z* (%): 606 (1, [M^+]), 571 (4, [M^+ – Cl], 479 (100, [M^+ – I]). The ^1H NMR spectrum of **7** shows two separated groups of septets (3.28, 3.64 ppm) and four groups of doublets (1.02, 1.12, 1.41, 1.42 ppm) for the respective isopropyl methine and methyl proton resonances of the Ar substituents, evidencing the asymmetric steric environment of the Ar isopropyl groups induced by Al–Cl and Al–I.

The X-ray crystal structural analysis of **7** showed a mononuclear compound with an aluminum center coordinated to the chelating β-diketiminato ligand and one Cl and one I atom in a distorted tetrahedral geometry. The molecular structure of **7** is shown in Figure 4 with selected bond lengths and angles. The terminal Al–I bond length (2.473(1) Å) is a little

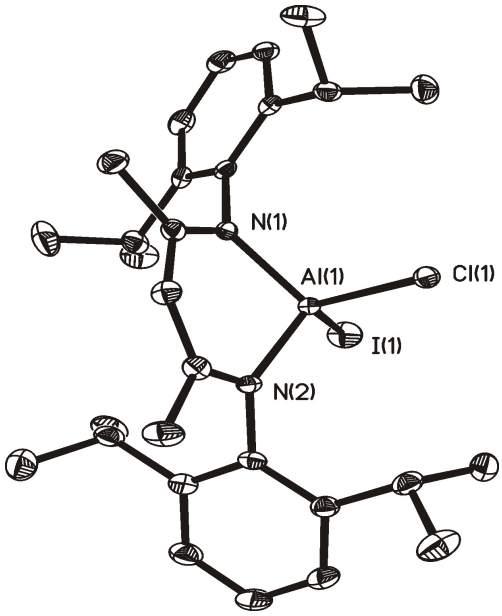
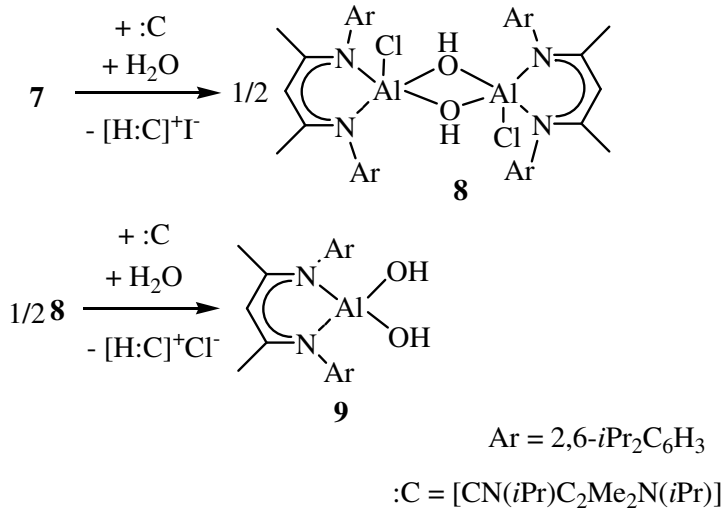


Figure 4. Molecular structure of **7**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.879(3), Al(1)–N(2) 1.863(3), Al(1)–Cl(1) 2.151(1), Al(1)–I(1) 1.473(1), N(1)–Al(1)–N(2) 100.04(12), Cl(1)–Al(1)–I(1) 111.82(6).

shorter than those in $LAlI_2$ (2.501(3), 2.543(3) Å),[77] and close to those in $[RAlI(\mu\text{-}I)]_2$ (R = 2,6-iPr$_2$C$_6$H$_3$N(SiMe$_3$)) (2.464(2) Å).[78] The Al–Cl distance (2.151(1) Å) is in good agreement with those in the terminal aluminum chlorides [3,5-tBu$_2$NCH=C(SiMe$_3$)·pz]AlCl$_2$ (2.135(1) Å), [3,5-tBu$_2$NCH=C(SiMe$_3$)·pz]AlCl(3,5-tBu$_2$pz) (2.153(1) Å),[79] and $[(C_7H_{13}N_2)AlCl]_2(\mu\text{-}O)$ (2.164(1) Å).[65]

The stepwise hydrolysis of compound **7** was first carried out with one equiv of H_2O in the presence of one equiv of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (abbreviated as **:C**) in toluene solution from 0 °C to room temperature (Scheme 7). The removal of solvent *in vacuo* followed by extraction with *n*-hexane gave partial hydrolysis product $[LAlCl(\mu\text{-}OH)]_2$ (**8**) in 70% yield. The mass spectrum of **8** indicates the monomeric composition (*m/z* (%):

496.3 (50, [M^+/2]), 478.3 (16, [M^+/2 – OH – 1], 461.3 (100, [M^+/2 – Cl]). However the ^{1}H NMR spectrum of **8** recorded at 200.13 MHz shows one septet (3.40 ppm) for the isopropyl methine resonances of the Ar substituents, while two groups of incompletely separated septets (3.42, 3.47 ppm) were observed at 500.13 MHz. These are markedly different from those observed in the NMR spectrum of compound **7** (3.28, 3.64 ppm) and imply a possible oligom



Scheme 7

-erization in solution. One singlet at 0.72 (in C_6D_6) alternatively 0.69 (in D_8-toluene) ppm could be assigned to the Al–μ-OH proton resonance comparable to the β-diketiminato aluminum dihydroxide LAl(OH)$_2$ (0.22 ppm).[76] One broad absorption centered at 3459 cm^{-1} corresponds to ν_{OH} in the IR spectrum of **8**.

The X-ray structural analysis unambiguously confirms compound **8** as a dimer in the solid state which is consistent with its solution behavior however in contrast to the EI-mass spectral results. The molecular structure of **8** is depicted in Figure 5 with selected bond lengths and angles. Each Al center is coordinated to one β-diketiminato ligand, one Cl, and two OH groups and adopts a distorted tetragonal-pyramidal geometry with the Cl atom located at the apical position and 2 N and 2 O atoms forming the basal plane (the least square plane Δ = 0.012 Å). The Al_2O_2 core is a perfectly planar four-membered ring due to the symmetry. The two H atoms of the OH groups are located within this plane (Δ = 0.009 Å). The Al–OH bond lengths (1.875(1), 1.886(1) Å) fall within the range of 1.787(3)–2.086(4) Å observed for

bridging aluminum hydroxides,[66-70] and are longer than the terminal ones in $LAl(OH)_2$ (1.697 (2) and 1.711 (2) Å)[75] and $[LAl(OH)]_2(\mu$-O) (1.738(3) and 1.741(3) Å).[80] The two Al–Cl bonds are *in trans* position arranged toward the $Al_2O_2H_2$ plane with bond distances (2.190(1) Å) slightly longer than that in **7**.

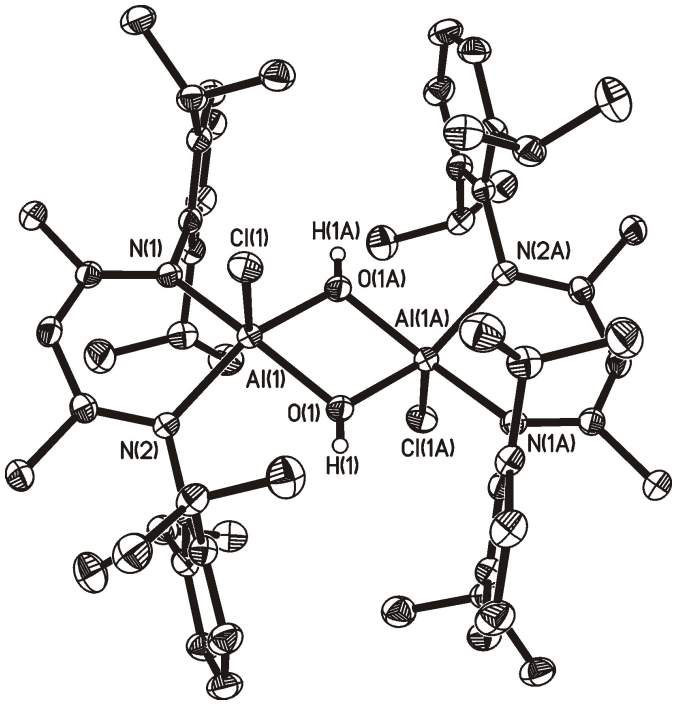
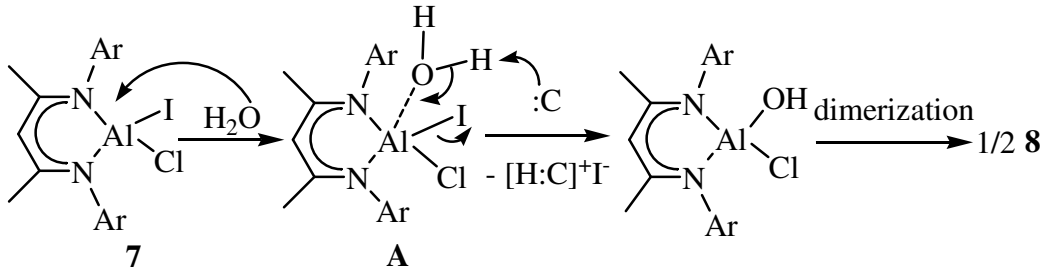


Figure 5. Molecular structure of **8**. H atoms in L are omitted for clarity. Selected bond lengths (Å) and angles (º): Al(1)–N(1) 1.977(1), Al(1)–N(2) 1.984(1), Al(1)–Cl(1) 2.189(1), Al(1)–O(1) 1.875(1), Al(1)–O(1A) 1.886(1), N(1)–Al(1)–N(2) 90.05(6), O(1)–Al(1)–O(1A) 72.46(7), N(1)–Al(1)–Cl(1) 92.91(6), N(2)–Al(1)–Cl(1) 100.90(5).

Attempts to obtain monomeric **8** by recrystallization from THF or by the use of THF as a solvent during the preparation were not successful, only the dimer **8** being formed. This behavior demonstrates the strong Lewis-acidic Al center in the monomeric LAlCl(OH) which leads to an association despite of the bulky ligand. This is in contrast to the monomeric species $LAlMe_2$,[81] $LAlI_2$,[77] $LAl(NH_2)_2$,[76] LAlMe(OH), and LAlClI.

It is interesting to mention that a direct interaction between **7** and *N*-heterocyclic carbene **:C** in THF solvent results in the generation of $[H{:}C]^+I^-$ as insoluble microcrystals, indicating the capability of proton abstraction of **:C** from the β-diketiminato ligand. (Analytic data for

compound [H**:C**]$^+$I$^-$: M.p. 173-174 ºC; ^{1}H NMR (500.13 MHz, CD_3CN, 298 K, ppm): δ 1.51 (d, 4 x 3 H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 2.23 (s, 2 x 3 H, C(CH_3)), 4.49 (sept, 2 x 1 H, $^3J_{HH}$ = 6.7 Hz, CH(CH$_3$)$_2$), 8.63 (s, 1 H, *H***:C**); EI-MS *m/z* (%): 181 (100, [H**:C**]$^+$), 128 (20, [I$^-$]); Anal. Calcd for $C_{11}H_{21}IN_2$ (*Mr* = 308.1): C, 42.87; H, 6.87; N, 9.09; I, 41,17. Found: C, 43.19; H, 6.83; N, 8.95; I, 40.45). The proton source of [H**:C**]$^+$I$^-$ might come from the β-methyl groups of the L ligand backbone.[82-84] Reference experiment of **:C** with H_2O in THF monitored by the ^{1}H NMR spectrum shows no characteristic resonance for [H**:C**]$^+$, and therefore indicates the incapability of **:C** to abstract a proton from uncoordinated H_2O. Accordingly we assume that the formation of **8** from the reaction of **7**, **:C**, and H_2O may proceed through the initial coordination of H_2O to aluminum (Scheme 8). This assumption is in accordance with the formation of $Al(OH_2)_6Cl_3$ from $AlCl_3$ by adding controlled amounts of water.[85] Comparable examples are the triarylaluminum water adduct $Mes_3Al{\cdot}OH_2{\cdot}nTHF$[69] and the structurally characterized $(C_6F_5)_3Al{\cdot}OH_2$.[86] The coordinated H_2O in **A** is deprotonated by **:C** to give the cation [H**:C**]$^+$ which subsequently combines with I$^-$ to form the insoluble [H**:C**]$^+$I$^-$. The generation of [H**:C**]$^+$I$^-$ rather than [H**:C**]$^+$Cl$^-$ apparently indicates the easier removal of I$^-$ compared to that of Cl$^-$.



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, :C = [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)]

Scheme 8

Further hydrolysis of **8** was accomplished with two equiv of H_2O and **:C** (Scheme 7). As expected the aluminum dihydroxide $LAl(OH)_2$ (**9**) was formed, however in a relatively low yield (25%). Such low yield might be due to the complete hydrolysis of partial **8**, which resulted in an insoluble aluminum oxide or hydroxide, and HL,[75] although a high yield was

achieved by the direct hydrolysis of $LAlCl_2$ in the presence of **:C**.[76] The hydrolytic procedure to **9** is similar to that for the conversion of **7** to **8**, but undergoes during the reaction a dissociation from dimeric **8** to monomeric **9** compared to an association from monomeric **7** to dimeric **8** in the first step of the hydrolysis.

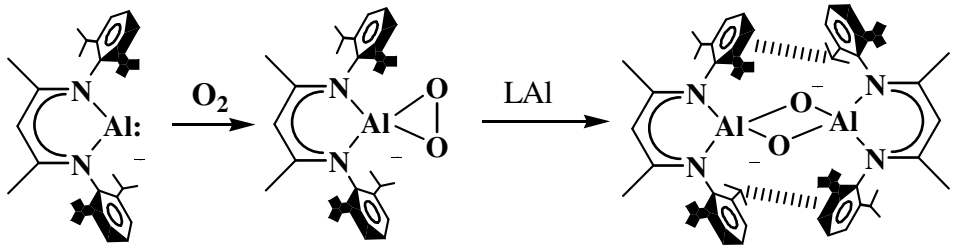
Thus, the synthesis of compound LAlClI (**7)** and its stepwise hydrolysis in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**:C**) has been described. The difference in the bond strength of Al–I and Al–Cl[87] allows the controlled stepwise hydrolysis. The deprotonation of the coordinated H_2O by **:C** under the formation of the insoluble $[H\mathbf{:C}]^+I^-$ or $[H\mathbf{:C}]^+Cl^-$ salts leads to $[LAlCl(\mu\text{-}OH)]_2$ **(8)** and $LAl(OH)_2$ (**9**), respectively, and demonstrates the powerful acceptor properties of the *N*-heterocyclic carbene. Accordingly, we were able to confirm this stepwise process, since there are no structural characterized precedents known containing the Al(OH)Cl moiety, although this type of intermediate is assumed in any hydrolysis product of $AlCl_3$. However the stepwise hydrolysis from **7** to **8** and finally to **9** is accompanied by an association followed by a dissociation process of LAlCl(OH) species. This observation is beyond our proposal during the direct hydrolysis of $LAl(Hal)_2$ (Hal = I, Cl) to **9**,[75] although it is not clear whether this pathway is involved in the latter formation. This may reflect the complexity of the stepwise hydrolysis process. Moreover the advantage of the $[H\mathbf{:C}]^+X^-$ (X = Cl, I) is that it can be completely recovered by filtration and in the presence of a strong base such as *t*BuOK quantitatively recycled to the *N*-heterocyclic carbene. This method of hydrolysis in the presence of *N*-heterocyclic carbene will be further applied to the preparation of Brönsted acidic sensitive systems.[85] Compound **8** contains Al–Cl and Al–OH functionalities, of which the former can react by metathesis, and the OH acting as a Brönsted acidic proton has been documented.[80] Further investigations on the functional reactions of **8** are in progress.

2.3. The Oxidative Reaction of Aluminum(I) Monomer LAl with Molecular Oxygen: A New Approach to Alumoxane

*Abstract: An alumoxane $[LAlO]_2$ (**10**) has been prepared from the oxidative reaction of aluminum(I) monomer LAl (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-i$Pr_2C_6H_3$) with molecular oxygen. The intense contacts of the $Al_2(\mu\text{-}O)_2$ unit bring the two oriented L closer together and causes a steric strain resulting in C–H···π interactions between one isopropyl group of one L and the aryl ring of another L. Further reaction of **10** with one equiv of H_2O resulted in the formation of an alumoxane hydroxide $[LAl(OH)]_2(\mu\text{-}O)$ (**11**), indicating a strain releasing process of **10**. An isomer of **10**, a C–H activatied aluminum hydroxide **13**, however, was obtained from the hydrolysis of a C–H activated large bulky aluminium amide **12**.*

There is great interest in alumoxanes since they can be used as active catalysts in the polymerization of epoxides, aldehydes, and olefins.[8-14] Furthermore, methylalumoxane (MAO) functioning as a highly active cocatalyst for group 4 metallocenes catalyzing ethylene and propylene polymerization[15-16] has been of remarkable industrial importance. In general, alumoxanes of formula $[RAlO]_n$ or $[R_2AlOAlR_2]_n$ (R = organic group) can be synthesized by the controlled hydrolysis of organoaluminum(III) compounds using water, or water containing metal salts,[66-67] and alternatively by the reaction of those compounds with oxygen containing species such as CO_2,[62] $RCONR_2$,[67] $MeCO_2H$,[88] PbO,[89] and $[Me_2SiO]_3$.[63] The reaction of R_2AlAlR_2 (R = $CH(SiMe_3)_2$) with Me_2SO generates the alumoxane $R_2AlOAlR_2$.[90] Alkylaluminum(III) compounds reacting with O_2 often undergo insertion reaction into the Al–alkyl bond and result in the formation of aluminum alkoxides and alkylperoxides.[5,91-94] In contrast, the reaction of organoaluminum(I) compounds with O_2 could lead to the oxidation of the aluminum center to yield alumoxane. Herein, we report on the reaction of aluminum(I) monomer LAl (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$)[95] with molecular oxygen and the isolation of an alumoxane $[LAlO]_2$ (**10**). **10** is further hydrolyzed to form alumoxane hydroxide $[LAl(OH)]_2(\mu\text{-}O)$ (**11**).

The toluene solution of LAl in the presence of O_2 between –78 ºC and room temperature, under stirring, changed slowly the color from red to orange, to yellow, and finally to almost colorless. At ca. –15 ºC **10** separated from the solution as a colorless crystalline solid (Scheme 9). The reaction of LAl with O_2 might proceed via an aluminum peroxide intermediate ($LAlO_2$), which further reacts with another molecule of LAl to afford **10**. It has been demonstrated that in the photolytically induced reactions of AlX/O_2 and $(AlX)_2/O_2$, an alumin



Scheme 9

-um peroxide $XAlO_2$ was mainly detected for the former and an oxide $XAl(\mu\text{-}O)_2AlX$ for the latter system by means of IR spectroscopy supported by quantum chemical calculations.[96-97] The formation of $XAl(\mu\text{-}O)_2AlX$ was proposed via an $Al(\mu\text{-}X)_2AlO_2$ intermediate. Moreover, peroxo complexes are also considered as potential intermediates or products during the oxidation of metals or metal clusters.[98-99] The occurance of this reaction at low temperatures indicates the high reactivity of LAl. The kinetic stabilization of LAl by ligand L allows its uncomplete oxidation in the range of –78 ºC to room temperature and generates **10** rather than the inorganic aluminum oxide. Furthermore the steric protection from the bulky Ar substituents at the N atoms of L allows the formation of the $Al_2(\mu\text{-}O)_2$ unit instead of a higher condensed Al–O product.

Compound **10** was obtained in high yield (80%). It melts at 314–315 ºC and the isotope distributed peaks at around *m/z* 920.4 (30%) in the EI-MS spectrum are assigned to the molecular ion [M^+]. **10** is soluble in hot aromatic solvents (toluene and benzene), whereas its solubility is poor at room temperature.

Quality X-ray single crystals were grown by cooling the hot toluene solution of **10** to room temperature within 24 h. The structural analysis reveals a dimer having crystallographic centro-symmetry (Figure 6). The central $Al_2(\mu\text{-}O)_2$ core is formed in a nearly perfect square (Al–O: 1.760(1), 1.763(1) Å; O–Al–O: 90.89(1)º; Al–O–Al: 89.11(1)º), the two chelating L ligands at each Al atom are oriented with puckering Al(1)N(1)C(2)C(3)C(4)N(2) and Al(1A)N(1A)C(2A)C(3A)C(4A)N(2A) rings respectively almost perpendicular (89.3º) to the square. The Al–O bond lengths are shorter than the predicted one (1.96 Å).[100] This may be due to π-interaction between the oxygen *p* orbitals and acceptor orbitals on aluminum which is discussed in a considerable number of publications.[101-104] These bond lengths can be comp

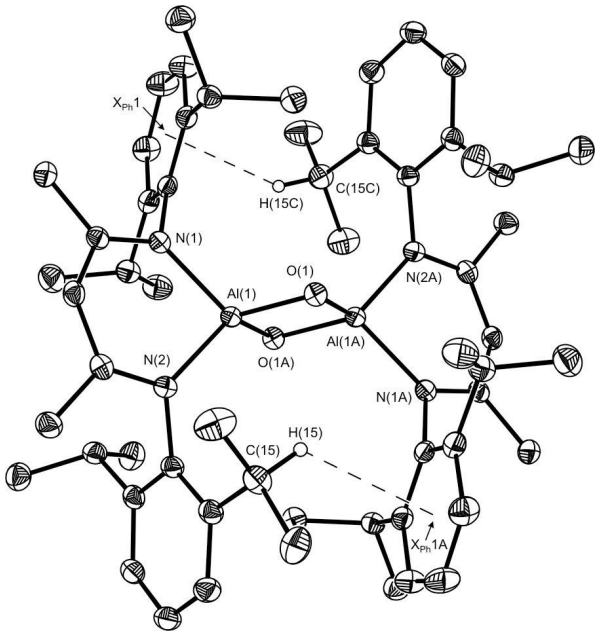


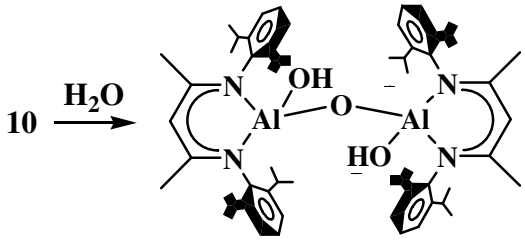
Figure 6. The molecular structure of **10**. Selected bond lengths [Å] and angles [º]: Al(1)–O(1) 1.760(1), Al(1)–O(1A) 1.763(1), Al(1)–N(1) 1.929(1), Al(1)–N(2) 1.943(1), Al(1)···Al(1A) 2.472(1), O(1)–Al(1)–O(1A) 90.86(5), Al(1)–O(1)–Al(1A) 89.14(5), N(1)–Al(1)–N(2) 94.40(5), C(15)–H(15) (56%)···X_{Ph}(1A) 2.71, C(15C)–H(15C) (44%)···X_{Ph}(1) 3.02.

-ared to those in compounds with four coordinate aluminum $R_2AlOAlR_2(ONMe_3)$ (R = $CH(SiMe_3)_2$, 1.753(3) Å) and $R_2(Me_3NO)AlOAlR_2(ONMe_3)$ (1.732(2)–1.739(2) Å).[105] However they are longer than those in $L^*AlO{\cdot}B(C_6F_5)_3$ (L^* = $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$) (1.659(3) Å),[106] $[(C_7H_{13}N_2)AlCl]_2(\mu\text{-}O)$

(1.677(1) Å),[107] and {*t*Bu$_2$Al[NH(Me)CH$_2$CH$_2$NMe$_2$]}$_2$(μ-O) (1.690(7)–1.714(7) Å),[74] as well as those in compounds **11** (1.694(3)–1.698(3) Å) and {[LAl(μ-O)]$_2$(μ-O)}AlMe (1.712(2) Å).[80] It is noteworthy that, based on the orientation of the two L, one isopropyl group of one L is facing toward the aryl ring of another L, and the two methyl substituents of this *i*Pr group are arranged on the same side of the aryl plane. This arrangement is in sharp contrast to the other ones. Such structural feature is remarkable when compared with those closely related compounds **11**, {[LAl(μ-O)]$_2$(μ-O)}AlMe,[80] [LAlCl(μ-OH)]$_2$ [108] and LAl(μ-S)$_2$AlL.[109] Obviously, due to the strong electronic interaction of Al and O atoms, the Al$_2$(μ-O)$_2$ unit is prone to intense contacts. These contacts, however, bring the two oriented L closer together and cause a steric strain giving a stable minimum configuration and resulting in C–H···π interactions between one isopropyl group of one L and the aryl ring of another L (C(15)–H(15) (56%)···X$_{Ph}$(1A) 2.71 Å, C(15C)–H(15C) (44%)···X$_{Ph}$(1) 3.02 Å). Similar structural features are discussed in compounds L$_2$M (M = Mg, Ca, Sr, Ba).[110] Accordingly, this indicates a considerable structural strain of **10**, and this strain is also reflected in little longer Al–N bond lengths (1.929(1), 1.943(1) Å) compared to those in **11** (1.911(3)–1.928(3) Å) and {[LAl(μ-O)]$_2$(μ-O)}AlMe (1.909(2)–1.930(3) Å).[80] In section 2.2., we isolated compound [LAlCl(μ-OH)]$_2$ from the stepwise hydrolysis of LAlClI in the presence of *N*-heterocyclic carbene (abbreviated as **:C**) as hydrogen halide acceptor. [LAlCl(μ-OH)]$_2$ presents a dimeric structure with Al–Cl and Al–μ-OH functionalities and further treatment of this compound with two equiv of **:C** functioning as a HCl acceptor in an attempt to approach **10**, or alternatively by the addition of *n*BuLi to eliminate LiCl and *n*BuH to the same target was not successful. The former resulted in no reaction and the latter led to an intractable mixture of products which was indicated by the EI mass spectrometry and proton NMR spectroscopy analysis. This may indicate the property of **10** that the functional changes using [LAlCl(μ-OH)]$_2$ as a precursor to approach **10** are energetically unfavored.

The NMR spectroscopic analysis of **10** clearly shows that this strained solid-state structure

is retained in solution. In the ^{1}H NMR spectrum the isopropyl groups give rise to four separated septets and eight doublets, and two sets of aromatic signals and two singlets for the methyl group of the backbone are also observed, indicating different steric environments of two Ar groups of the LAl moiety. Moreover, one septet and one doublet of those appear at higher field (2.63 and 0.22 ppm) in comparison to the resonances in a series of related compounds **11**, {[LAl(μ-O)]$_2$(μ-O)}AlMe, and [LAlCl(μ-OH)]$_2$ (4.14–3.06, 1.58–0.72 ppm).[80,109] It is clearly seen that, in view of the structure of **10**, the corresponding methine (CH) and methyl (CH_3) groups are shielded due to the ring current effect within the aryl groups,[111] and this is typical for groups involved in C–H···π interaction (Figure 6). The ^{13}C{^{1}H} NMR data also shows the methine carbon resonance at high field (71.4 ppm).



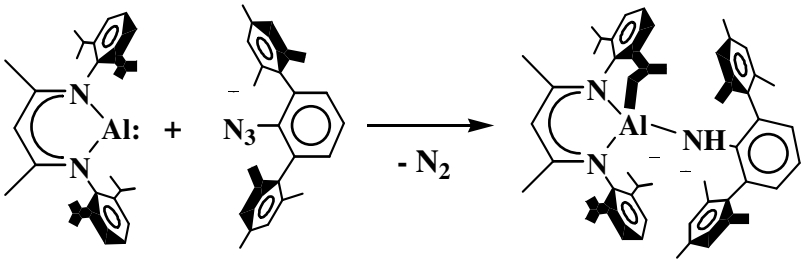
11

Scheme 10

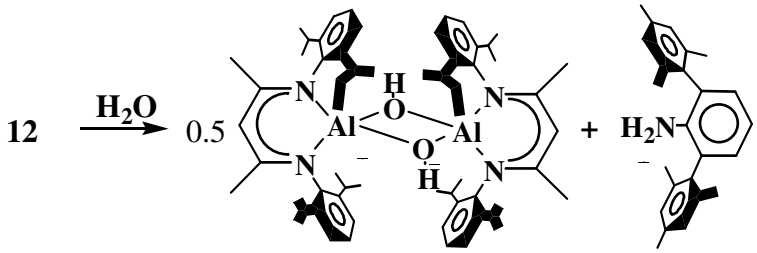
It is interesting to note that when this sample was kept at room temperature for one month, the NMR analysis showed that the proton resonances at high field (one septet and one doublet) disappeared as well as the methine carbon resonance, and the data of the ^{1}H NMR spectrum can be identified like that of compound **11** including a small amount of free ligand. The transformation of **10** to **11** could be considered as a further hydrolysis of **10** due to the possible penetration of small amounts of moisture to the sample through the seal (Scheme 10). Nevertheless, the reaction of **10** with stoichiometric amounts of water was performed, and colorless crystals of **11**·1.5 *n*-hexane were obtained and confirmed by X-ray structural analysis.

The reaction of LAl with N_3Ar' in the presence of a small amount of H_2O resulted in the

formation of a C–H activated aluminum hydroxide **13**, an isomer of **10**. This reaction can be reproduced. The reaction of LAl with a large bulky azide N_3Ar which has shown two types of intramolecular addition to an Al=N multiple bond species will be detailed in section 2.8. The respective isolation of **12**, **13**, and H_2NAr' indicates the partly hydrolysis of **12** to **13** at low temperature (Scheme 11). The Al–N bond imposed by the bulky Ar' in **12** might preferentially react with H_2O to form **13**, an isomer of **10**. **12**, **13** and H_2NAr' are characterized by spectral analysis, and **12** and **13** are further confirmed by X-ray measurement.



12



13

Scheme 11

The molecular structures of **12** and **13** are viewed in Figures 7 and 8. The structural analysis of **13** shows the same composition like that of **10** but with five coordinate Al and an $Al_2(\mu\text{-}OH)_2$ non-planar core instead (Δ = 0.1009 Å). The parameters of Al–C (1.988(2) Å (av)) and $C_{activated}$–C (1.552(2) Å (av)) exhibit normal single bond distances, and those of $Al_2(\mu\text{-}OH)_2$ (Al–O: 1.879(1) Å (av); O–Al–O: 73.88(6)° (av); Al–O–Al: 103.40(1)° (av)) are comparable to those in $[LAlCl(\mu\text{-}OH)]_2$ (Al–O: 1.880(1) Å (av); O–Al–O: 72.46(7)° (av)).[14a] These data compared with those of **10** indicate less interference within **13** than in **10**. The NMR (Al–CH_2: δ –1.69 (t), –0.35 (dd) ppm; Al–μ-OH: 0.29 (s) ppm) and IR spectral data

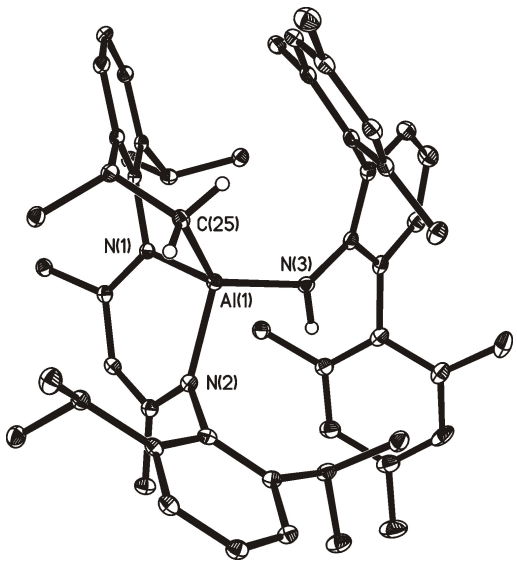


Figure 7. Molecular structure of **12**. H atoms except for Al–CH_2 and Al–NH are omitted for clarity. Selected bond lengths (Å) and angles (º): Al(1)–N(1) 1.930(1), Al(1)–N(2) 1.926(2), Al(1)–N(3) 1.840(1), Al(1)–C(25) 1.967(2), C(25)–C(24) 1.555(2), N(1)–Al(1)–N(2) 98.12(6), N(1)–Al(1)–N(3) 113.83(6), N(2)–Al(1)–N(3) 101.98(7), N(3)–Al(1)–C(25) 124.18(7).

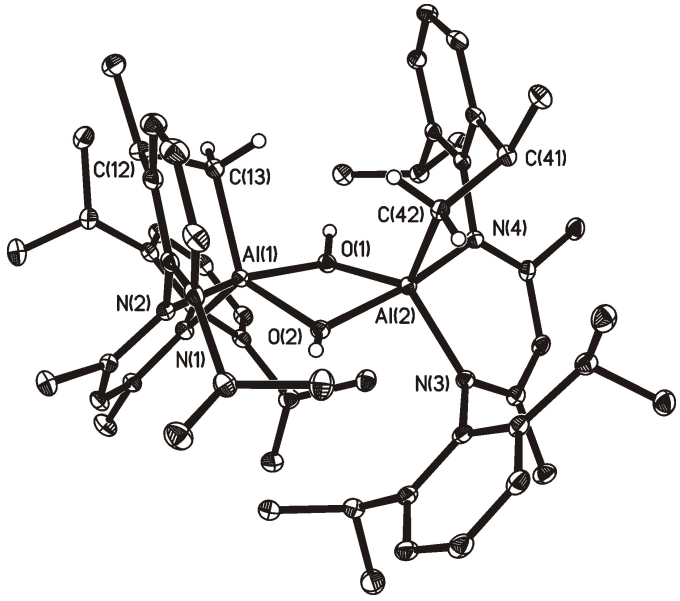


Figure 8. Molecular structure of **13**. H atoms except for Al–CH_2 and Al–OH are omitted for clarity. Selected bond lengths (Å) and angles (˚): Al(1)–O(1) 1.910(1), Al(1)–O(2) 1.850(1), Al(1)–C(13) 1.986(2), C(13)–C(12) 1.549(2), Al(2)–O(1) 1.852(1), Al(2)–O(2) 1.905(1), Al(2)–C(42) 1.989(2), C(42)–C(41) 1.554(3), Al(1)···Al(2) 2.950(1), O(1)–Al(1)–O(2) 73.84(6), Al(1)–O(2)–Al(2) 103.54(6), O(2)–Al(2)–O(1) 73.92(6), Al(2)–O(1)–Al(1) 103.25(6)

(Al–μ-OH: ν 3400 (br) cm^{-1}) also confirm the functionalities of **13**.

Although **10** does not contain three coordinate Al centers which are proposed to have strong Lewis acidity and are vital for catalytic activity, the notably structural character of **10** prompted us to test its cocatalytic property for the dimethylzirconocene polymerization of ethylene in toluene solution at either 25 or 80 ºC. However, no activity was observed. Moreover, no reaction occurred between **10** and Cp_2ZrMe_2.

In conclusion, the oxidative reaction of aluminum(I) monomer LAl with molecular oxygen has been shown. This reaction type exhibits the O_2 oxidation of a central metal to yield alumoxane $[LAlO]_2$ (**10**), the hitherto unknown species, and represents a new synthetic approach to alumoxane. Compound **10** further reacts with one molecule of water to form alumoxane hydroxide $[LAl(OH)]_2(\mu$-O) (**11**). Although **11** has been known and prepared by another route,[80] this reaction may proceed through the coordination of H_2O to the aluminum center. A further proton transfer from the coordinated H_2O molecule results in the ring opening of the $Al_2(\mu$-$O)_2$ unit under the formation of terminal Al–OH functionalities, this implies a strain releasing process from **10** to **11**. A further application of proton transfer using EH_n (E = S, Se, Te, n = 2; E = N, P, As, Sb, n = 3) molecules and **10** to yield the unknown $Al–EH_{n-1}$ species is currently under investigation in our group.

2.4. Reactions of Aluminum(I) Monomer LAl with Imidazol-2-ylidene and Diphenyldiazomethane: A Hydrogen Transfer of the L Ligand to the Aluminum Center and a Formation of a Diiminyl Aluminum Compound $LAl(N{=}CPh_2)_2$

*Abstract: The solid-state reaction of LAl and imidazol-2-ylidene at elevated temperature (120 °C) yielded the aluminum monohydride N-heterocyclic carbene adduct [HC{C(CH₂)NAr}(CMeNAr)]AlH[CN(R)C₂Me₂N(R)] (R = iPr (**14**), Me (**15**)). Compounds **14** and **15** have been characterized by spectroscopic (IR, ^{1}H, and ^{13}C NMR), mass spectrometric, and elemental analyses, and **14** was further characterized by X-ray structural analysis. These experimental data indicate that the Al–H bond is formed by hydrogen migration from one of the methyl groups of the β-diketiminato ligand backbone. The reaction of LAl with equivalent amounts of diphenyldiazomethane afforded the diiminyl aluminum compound LAl(N=CPh₂)₂ (**16**), while with an excess diphenyldiazomethane resulted in the formation of Ph₂C=N–N=CPh₂. This suggests that the Ph₂C=N–N=CPh₂ is initially generated and then further reacts under oxidative addition to yield **16**.*

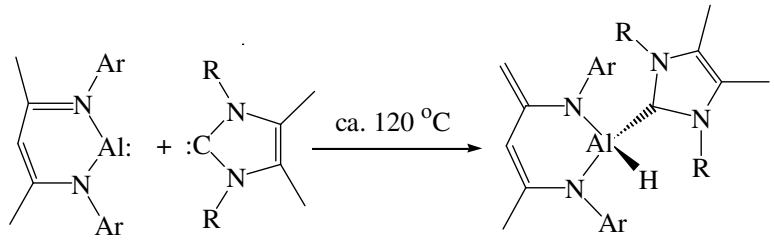
Monovalent Group 13 species are of considerable interest not only due to their syntheses, structures, and theoretical investigations,[112-113] but more due to their reactivity.[114] In the last decade, a variety of new reactions has been intensively explored generating the tetrameric aluminum(I) compounds.[115-120] Compound $(Cp^*Al)_4$ was reported to have a remarkable tendency to dissociate in solution and give a monomeric fragment in the gas phase.[121-122] The reactions involving such species have also been investigated to some extent and a number of novel compounds were isolated and structurally characterized.[123-127] Recently, we have prepared the first monomeric aluminum(I) LAl (L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) stable at room temperature.[95] Ab initio calculations show that this monomer possesses a nonbonded electron pair at the central two coordinated Al atom and is isoelectronic with a singlet carbene. Subsequent examination of LAl with organic azides at low temperature or with P_4 at room temperature indicates its reactivity, leading to the formation of a five-

membered AlN_4 heterocycle $LAl[(NSiMe_3)_2N_2]$, a monomeric aluminum imide LAl(N-2,6-$Trip_2C_6H_3$) (Trip = 2,4,6-*i*$Pr_3C_6H_2$), and a sandwich compound $(LAl)_2P_4$ containing a P_4^{4-} unit.[129-131] These results are markedly different from those in which $(Cp^*Al)_4$ is used in related reactions. Obviously, the steric and electronic stabilization from the bulky *β*-diketiminato ligand enables its monomeric nature and therefore its unique chemical behaviour, and allows further investigation of its reactivity.

Imidazol-2-ylidene is a stable neutral *N*-heterocyclic carbene which has been prepared in recent years.[132] The diphenyldiazomethane can be used as an effective precursor for the generation of transient $:CPh_2$.[133-135] The reaction of imidazol-2-ylidene with monovalent Group 13 compounds is only reported for InBr, in which a disproportionation is observed.[136] More recently, a handful of reactions involving imidazol-2-ylidene with trivalent Group 13 species have been investigated, and herein the *N*-heterocyclic carbene functions as a Lewis base.[137-141] Corresponding reactions of diphenyldiazomethane with Group 13 element(I) species have not been described so far. We now report on the reaction of LAl with imidazol-2-ylidene and diphenyldiazomethane, respectively. The formation of the aluminum monohydride *N*-heterocyclic carbene adduct of composition $[HC\{C(CH_2)NAr\}(CMeNAr)]AlH[CN(R)C_2Me_2N(R)]$ (R = *i*Pr (**14**), Me (**15**)) indicates a hydrogen transfer from the L ligand to the aluminum center. The formation of a diiminyl aluminum compound $LAl(N{=}CPh_2)_2$ (**16**) might proceed through the initial generation of $Ph_2C{=}N{-}N{=}CPh_2$ followed by its oxidative addition to LAl.

The initial reaction of LAl with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene was conducted in toluene within the temperature range from 25 to 80 °C. However due to the low solubility of the *N*-heterocyclic carbene, this reaction was not successful. Therefore both starting materials were treated in the solid-state at 120 °C for 5 h. The softening of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene and a subsequent color change of LAl from red black to light yellow were observed. An extraction of the product with hot toluene and

keeping the eluate at room temperature afforded crystalline compound [HC{C(CH$_2$)NAr}(CMeNAr)]AlH[CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (**14**, Scheme 12).



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ (R = *i*Pr **14**, Me **15**)

Scheme 12

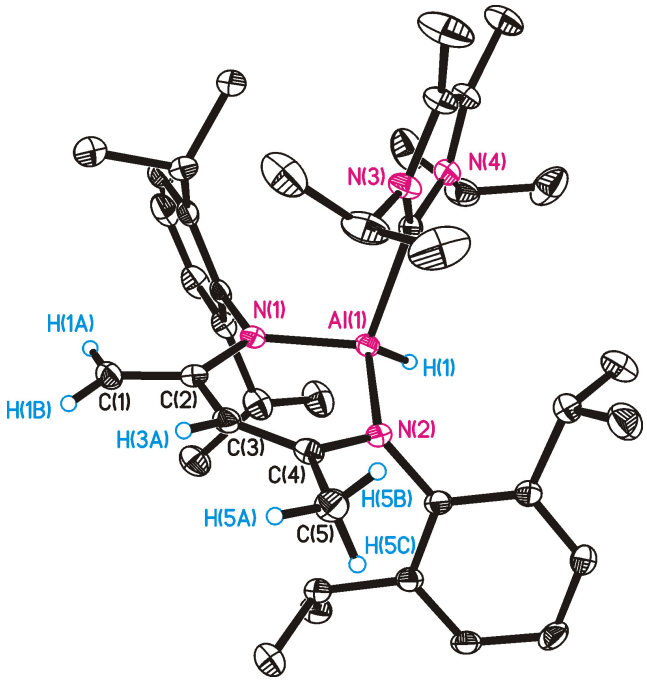


Figure 9. Molecular structure of **14**. H atoms in Ar and **:C** groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.853(2), Al(1)–N(2) 1.844(3), Al(1)–C(30) 2.088(3), Al(1)–H(1) 1.40, N(1)–C(2) 1.411(3), N(2)–C(4) 1.413(3), C(1)–C(2) 1.363(4), C(2)–C(3) 1.458(4), C(3)–C(4) 1.351(4), C(4)–C(5) 1.507(4), N(1)–Al(1)–N(2) 102.05(6), C(30)–Al(1)–H(1) 106.4.

Compound **14** is colorless and soluble in hot toluene and benzene while sparingly soluble in *n*-hexane and pentane. It has been characterized by spectroscopic and elemental analyses. The mass spectrum exhibits the molecular ion of **14** { *m/z* (%) = 624 (5) [M^+], 609 (40) [M^+ -

Me], 581 (100) [M^+ - *i*Pr]}. The ^{1}H and ^{13}C NMR spectra recorded in C_6D_6 are consistent with a pseudo tetrahedral geometry and *Cs* symmetry about aluminum, which give rise to six isopropyl C*H* resonances and twelve diastereotopic splitted isopropyl CH_3 resonances due to the chiral environment of the Al center. It is noted that the proton resonance of β-CH_3 (δ 1.72 ppm) at the L ligand backbone is indicative for 3H, while two other singlets are observed downfield (δ 3.98 and 3.30 ppm) for (1 + 1) H. The former corresponds to the normal terminal CH_3–C group, and the latter is assigned to the terminal CH_2=C group which gives rise to two non-equivalent protons due to the restricted rotation about the C=C double bond. One broad proton resonance centered at 4.80 ppm is characteristic for aluminum hydrides,[29] and the IR spectrum exhibits a single band at 1809 cm^{-1} for Al–H absorption.[142]

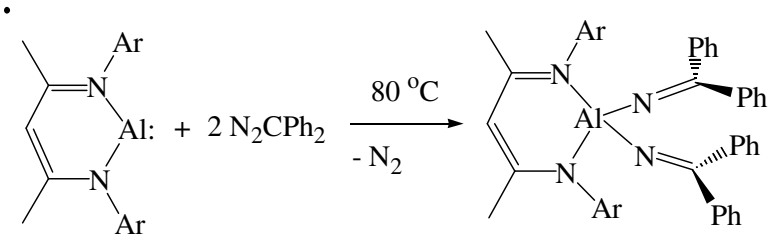
Complex **14** has also been characterized by X-ray structural analysis. The quality of the crystals by several recrystallizations from different solvents gave no improvement in the refinement of the structure. Nonetheless, the structural solution of **14** offers important structural informations which are in agreement with its spectral analysis. The molecular structure of **14** is shown in Figure 9 with selected bond lengths and angles. Compound **14** is monomeric and the central Al atom adopts a distorted tetrahedral geometry. The Al–N bond lengths (1.844(3), 1.853(2) Å) appear the shortest compared to those Al–$N_{\beta\text{-diketiminato}}$ (1.875(4)–1.957(2) Å),[21,75,80,95] and are closer to those found in diamide aluminum monohydride [ArN(CH_2)$_3$NAr]AlH(NMe_3) (1.820(1), 1.828(1) Å).[142] In the ligand backbone, the terminal C–C bond distances (C(4)–C(5), 1.507(4) Å; C(1)–C(2), 1.363(4) Å) are indicative for a single and double bond character, respectively, as well as the others within the backbone (C(2)–C(3), 1.458(4) Å; C(3)–C(4), 1.351(4) Å). The adjacent N–C bonds (1.411(3), 1.413(3) Å) are located between N–C double and single bonds.

Obviously, the Al–H hydrogen comes from one of the terminal methyl groups of the L ligand. However, such hydrogen transfer via proton, hydrogen radical, or hydride is not clear.

The reaction of the LAl with less bulky *N*-substituted 1,3,4,5-tetramethylimidazol-2-

ylidene was also performed in a similar manner (method A) like the preparation of **14** to investigate the steric bulk on the reaction product. As a result, [HC{C(CH_2)NAr}(CMeNAr)]AlH[CN(Me)C_2Me_2N(Me)] (**15**) was obtained in a relatively low yield. All the spectroscopic (IR, EI mass, ^{1}H and ^{13}C NMR) data confirm the analogue structural arrangement like that of **14** with 1,3,4,5-tetramethylimidazol-2-ylidene as a ligand.

In the majority of organic and organometallic reactions, diphenyldiazomethane is used as an effective precursor for the generation of transient :CPh_2 carbene.[133-135] Therefore, it was selected as another electron-rich species for the reaction with LAl. However, treatment of LAl with 2 equivalents of N_2CPh_2 under heating unexpectedly afforded LAl(N=CPh_2)$_2$ (**16**, Scheme 13), the first example of a diiminyl aluminum compound. When LAl was treated with an excess of N_2CPh_2 under the same condition Ph_2C=N–N=CPh_2 was isolated. The azine Ph_2C=N–N=CPh_2 was obtained as colorless crystals with a melting point of 174 ºC and the spectroscopic data (EI mass, IR, ^{1}H and ^{13}C NMR) and elemental analysis confirmed the composition. It is well-known that many salts and complexes of Cu(I) and Cu(II) are used as catalysts for the decomposition of diphenyldiazomethane. The reaction of LAl and diphenyldiazomethane to give Ph_2C=N–N=CPh_2 may indicate that the LAl plays more likely a catalytic role[143-144] Therefore we assume that the formation of **16** might proceed via the initial generation of Ph_2C=N–N=CPh_2 followed by its oxidative addition to LAl. In order to testify the possibility of the latter step, a toluene solution of LAl with equivalent amounts of Ph_2C=N–N=CPh_2 was conducted under reflux and complex **16** was formed as expected in an almost quantitative yield. A reaction procedure is described here. A mixture of equivalent amounts of LAl and Ph_2C=N–N=CPh_2 in toluene (20 mL) was allowed slowly to heat to reflux and kept for 3 h. After cooling to room temperature, the solution was dried in vacuum and the residue was washed with *n*-hexane (5 mL) to give an almost quantitative orange-yellow crystalline solid (yield, > 90%). The melting point and the spectroscopic data (EI mass and IR) are essentially the same as those of **16**.



16

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Scheme 13

Complex **16** is an orange-yellow crystalline solid and thermally stable as indicated by its high melting point (344-346 ºC). The most intense ion in the EI mass spectrum appears at *m/z* 624 [M^+ - NCPh$_2$], and the peak at *m/z* 805 (20%) is assigned to the molecular ion [M^+].

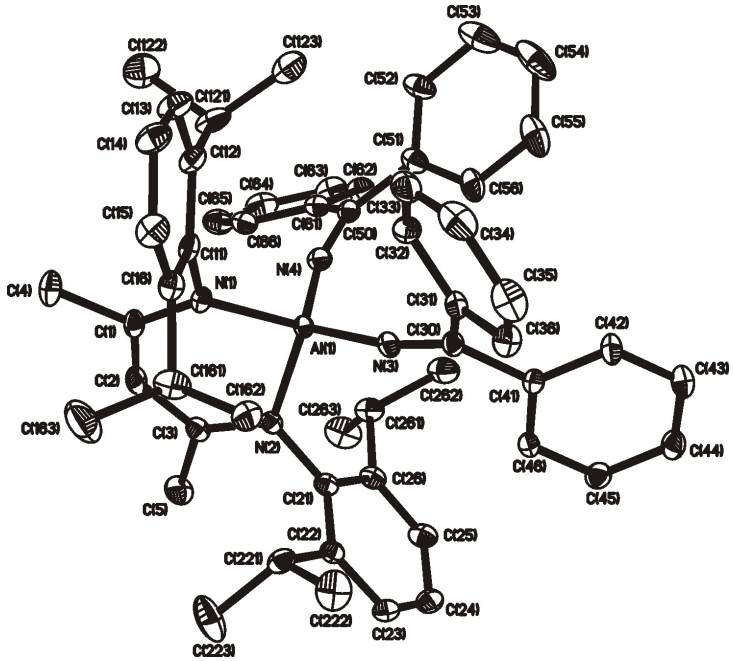


Figure 10. Molecular structure of **16**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Al(1)–N(1) 1.901(4), Al(1)–N(2) 1.899(4), Al(1)–N(3) 1.774(4), Al(1)–N(4) 1.785(4), N(3)–C(30) 1.249(6), N(4)–C(50) 1.269(6), N(1)–Al(1)–N(2) 97.23(18), N(3)–Al(1)–N(4) 116.1(2), C(30)–N(3)–Al(1) 169.4(4), C(50)–N(4)–Al(1) 163.4(5).

X-ray quality single crystals of **16** were grown in 1:1 solvent mixture (*n*-hexane, ether) at 4 ºC for 2 d. The structural analysis unambiguously ascertains the composition of **16**. The molecular structure is viewed in Figure 8 with selected bond lengths and angles. The central

Al atom is bound to two β-diketiminato nitrogen and two iminyl nitrogen atoms. The AlN_4 core exhibits a distorted tetrahedral geometry with *trans* N–Al–N angles ranging from 97.23(18)º to 117.6(2)º. The Al–$N_{\beta\text{-diketiminato}}$ bond lengths (1.899(4), 1.901(4) Å) are falling in the expected range (1.875(4)–1.957(2) Å). However, the Al–N_{iminyl} distances (1.774(4), 1.785(4) Å) are the shortest among those found in four coordinated Al–N complexes.[145] Comparable Al–N bond lengths are only observed in three coordinated $Trip_2AlN(H)Dipp$ (1.784(3) Å),[146] $[MeAlNDipp]_3$ (1.782(4) Å)[147] and $Al[N(SiMe_3)_2]_3$ (1.78(2) Å).[148] Surprisingly, the N–C distances of the iminyl group (1.249(6), 1.269(6) Å) are shorter compared to that of a carbon-nitrogen double bond.[149] The short Al–N_{iminyl} bond can be considered to be highly ionic, and the shortening of the N=C bond may be due to a charge delocalization over the phenyl groups. The Al(1)–N(4)–C(50) (163.4(5)º) and Al(1)–N(3)–C(30) (169.4(4)º) angles show the less bent arrangement of the Al–N=C group. The observation of two sets of resonances for the iminyl phenyl rings in the ^1H and ^{13}C NMR spectra suggests a restricted rotation of phenyl rings around the N=C bond. This is confirmed by the high temperature proton NMR spectral analysis (40, 60, and 80 ˚C), where two corresponding sets of such resonances are always observed.

To sum up, the reaction of the aluminum(I) monomer LAl with imidazol-2-ylidene and diphenyldiazomethane, respectively, afforded the new compounds $[HC\{C(CH_2)NAr\}(CMeNAr)]AlH[CN(R)C_2Me_2N(R)]$ (R = *i*Pr (**14**), Me (**15**)) and $LAl(N{=}CPh_2)_2$ (**16**). This further shows the unique reaction behaviour of LAl, and exhibits its properties of a carbene analogue. Inspired by these results, we are now exploring the reaction of LAl with metal carbonyl complexes to compare the electronic equivalence of LAl with CO.

2.5. A Rearrangement of Azobenzene by Interaction with an Aluminum(I) Monomer LAl

*Abstract: Reaction of LAl or LAl[η^2-$C_2(SiMe_3)_2$] (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-i$Pr_2C_6H_3$) with azobenzene both afforded a five-membered ring compound LAl[N(H)-o-C_6H_4N(Ph)] (**17**). In the formation of **17** a three-membered intermediate LAl(η^2-N_2Ph_2) (**A**) is suggested by [1 + 2] cycloaddition reaction, **A** is not stable and further rearranges to **17**. The DFT calculations on comparable compounds with modified L' (L' = HC[(CMe)(NPh)]$_2$) show that the complexation energy of the reaction of L'Al with azobenzene to L'Al(η^2-N_2Ph_2) is ca. –39 kcal/mol, and the best estimate of the energy difference between L'Al(η^2-N_2Ph_2) and L'Al[N(H)-o-C_6H_4N(Ph)] is –76 kcal/mol.*

The reactions of Group 13 metal(I) tetramers $(RM)_4$ (R = organic group, M = Al, Ga, In) with unsaturated molecules (H_2C=C(Me)–C(Me)=CH_2, PhC(O)–C(O)Ph, RN=C(H)–C(H)=NR, R = Me, *i*Pr)[150-153] evidence the trapping of the corresponding monomer RM, and meanwhile present an interesting oxidative addition of compounds with unsaturated bonds to low-valent metal centers.[114] This leads to heterocyclic compounds containing novel heavier main group elements which have the potential application in pharmaceutical, agrochemical, and material science.[154] We have recently prepared the aluminum(I) monomer LAl (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$) which has a singlet carbene character.[95] The reductive coupling reaction of $LAlI_2$ with potassium in the presence of alkynes has shown a [1 + 2] cycloaddition to yield aluminacyclopropene LAl[η^2-C_2(R)R'] (R = R' = $SiMe_3$, Ph; R = Ph, R' = $SiMe_3$).[155] A direct coupling reaction between LAl and alkyne ($Me_3SiC{\equiv}CC{\equiv}CSiMe_3$) is subsequently realized to form LAl[η^2-$C_2(SiMe_3)(C{\equiv}CSiMe_3)$]. In this context we are interested in the interaction of the Al(I) center with compounds containing a N=N double bond. The reaction of LAl or LAl[η^2-$C_2(SiMe_3)_2$] with azobenzene both unexpectedly resulted in the formation of a five-membered ring complex LAl[N(H)-*o*-C_6H_4N(Ph)] (**17**). Compound **17** contains a N(H)-*o*-C_6H_4N(Ph) moiety which presents an

isomerized azobenzene. Obviously, a rearrangement of azobenzene is occurring by interacting with LAl.

Upon stirring a toluene solution of LAl and azobenzene at elevated temperature (80 ºC) for 5 h, the red color changed to orange. Partial removal of the solvent in vacuum and addition of *n*-hexane led to the crystallization of **17** at 4 ºC as orange crystals in good yield. An alternative route to **17** was investigated by the reaction of LAl[η^2-$C_2(SiMe_3)_2$] with azobenzene in the temperature range from –50 ºC to room temperature. The result indicated that LAl[η^2-$C_2(SiMe_3)_2$] could be used as a good precursor for LAl.

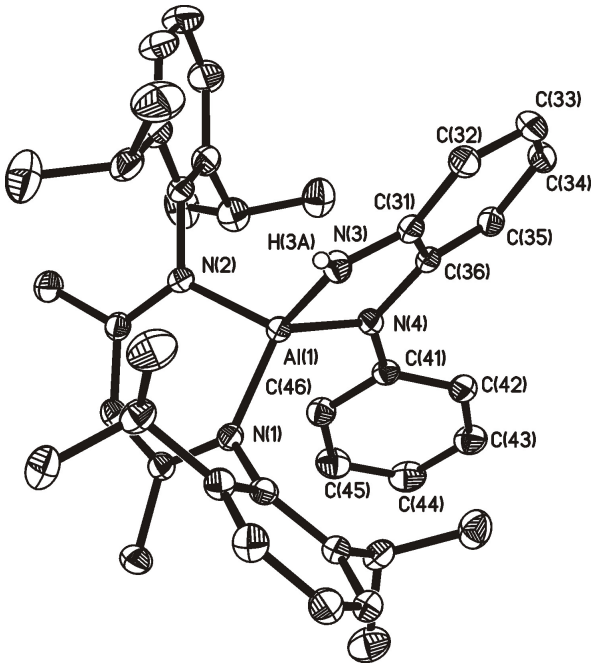
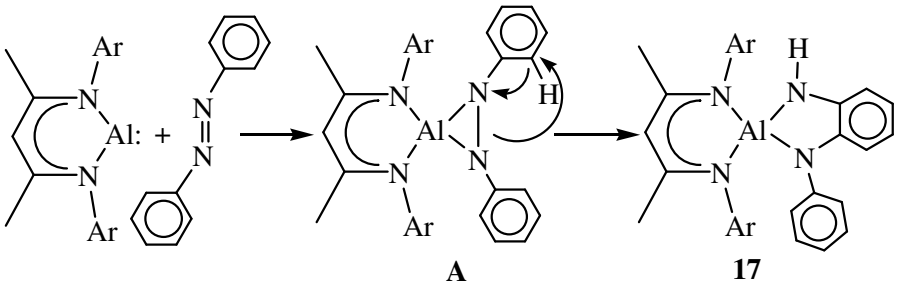


Figure 11. Molecular structure of compound **17**. The hydrogen atoms of the C–H bonds are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) 1.862(1), Al(1)–N(2) 1.893(1), Al(1)–N(3) 1.807(2), Al(1)–N(4) 1.847(1), N(3)–C(31) 1.386(2), C(31)–C(36) 1.429(2), C(36)–N(4) 1.420(2), N(1)–Al(1)–N(2) 97.68(6), N(3)–Al(1)–N(4) 90.39(6), Al(1)–N(3)–C(31) 109.86(10), N(3)–C(31)–C(36) 115.57(14), C(31)–C(36)–N(4) 113.40(10), C(36)–N(4)–Al(4) 108.44(10).

Compound **17** is thermally stable, as indicated by its high melting point (260–261 ºC) and its most intense molecular ion peak (m/z (%): 626 (100, [M^+]) recorded in EI-mass spectrum.

17 has been fully characterized by spectroscopic, analytical and X-ray single crystal measurements.

The molecular structure of **17** is viewed in Figure 11 with selected bond lengths and angles. The central Al atom is involved as part of two fused five- (AlN_2C_2) and six-membered (AlN_2C_3) rings. The corresponding AlN_4 core appears in a distorted tetrahedral geometry. The Al–N bond lengths within the AlN_2C_2 ring are 1.807(2) Å (Al–N(H)) and 1.847(1) Å (Al–N(Ph)), respectively, and can be compared with those of the AlN_4 ring complex (1.815(2), 1.851(2) Å).[129] The Al–$N_{\beta\text{-diketiminato}}$ bond lengths (1.893(1) and 1.862(1) Å) fall in the range (1.874(1)–1.959(3) Å) observed for four-coordinate β-diketiminato aluminum compounds,[155-156] although one bond is a little shorter than these values. The AlN_2C_2 ring is nearly planar (Δ = 0.0719 Å) and this planar character can be extended to the adjacent disubstituted phenyl group (Δ = 0.0816 Å). It is interesting to note that, within the AlN_2C_2 ring, the C(31)–C(36) bond length (1.429(2) Å) is longer compared to the remaining ones of the phenyl ring (1.382(2)–1.393(2) Å). This obviously contributes to a ring formation of AlN_2C_2. The phenyl groups involved in different structural environments (disubstituted C_6H_4, N(Ph), Ar) exhibit diverse resonances for the aromatic protons in the ^{1}H NMR spectrum of **17**. An unambiguous assignment of the resonances was not possible. The NH resonates at δ 3.06 (s) and in the IR spectrum the absorption at 3220 cm^{-1} is assignable to ν_{NH}.



A **17**

Ar = 2,6-*i*$Pr_2C_6H_3$

Scheme 14

The reaction of LAl with azobenzene may initially proceed through a LAl(η^2-N_2Ph_2) (**A**) intermediate which was formed by [1 + 2] cycloaddition reaction. **A** is not stable due to the

high strained metal containing three-membered AlN_2 ring, and therefore rearranges by cleaving the N–N bond under migration of a hydrogen from an *ortho* position of one adjacent phenyl ring to yield **17** (Scheme 14). Similar structural compounds like **A** are known for transition and lanthanide metals, in which the different electronic interaction modes (π bonds and one electron transfer) are discussed.[157-159] A three-membered AlN_2 heterocycle bearing an exocyclic N=C double bond at one of the two N atoms has also been reported.[160] Correspondingly, an easy cleavage of the N–N bond and the rearrangement of the adjacent *ortho* phenyl hydrogen of azobenzene were also observed in the reaction of an FeH-containing active site with azobenzene,[161-162] in a cyclometalation[163-166] and a substitution[167] reaction.

A further insight into this proposed mechanism is gained from theoretical calculation.[168] The DFT (Density Funtional Theory) calculations are performed by analyzing the energy difference of products and reactants in reaction system of L'Al and PhNNPh to L'Al(η^2-N_2Ph_2), and then to L'Al[N(H)-*o*-C_6H_4N(Ph)], where L' is modified as HC[(CMe)(NPh)]$_2$ for simplicity of calculation and their corresponding geometries are optimized according to the real structures or related ones at BP86/TZVP level with RI approximation (L'Al to LAl, PhNNPh in *cis* position, L'Al(η^2-N_2Ph_2) to LAl(η^2-C_2Ph_2) but a N–N single bond, and L'Al[N(H)-*o*-C_6H_4N(Ph)] to LAl[N(H)-*o*-C_6H_4N(Ph)]) using TURBOMOLE 5.5 program. The computed results show that the complexation energy of the initial reaction of L'Al with azobenzene to L'Al(η^2-N_2Ph_2) (here L' is modified as HC[(CMe)(NPh)]$_2$ for simplicity of calculation) is ca. –39 kcal/mol (that is D_{298} (Al–η^2-N_2) = 39 kcal/mol). This indicates a reasonable possibility of **A** as an intermediate in the reaction of LAl with azobenzene. The value of –39 kcal/mol is even lower than that calculated for the complexation energy of LAl with alkyne (ca. –21 kcal/mol) using the same method.[156] When L'Al(η^2-N_2Ph_2) is further converted to L'Al[N(H)-*o*-C_6H_4N(Ph)], a best estimate of the energy difference between these two isomers is –76 kcal/mol. This suggests an energetically favored stable rearrangement, and

is also in agreement with the rearrangement of a three- to five-membered ring. Furthermore, the D_{298} (Al–η^2-N_2) value is comparable to that of the Al–N bond strength in donor-acceptor $H_3Al{\cdot}NH_3$ species predicted by *ab initio* studies with zero-point vibrational energy correction (D_{298} (Al–N) = 26 kcal/mol).[169] This implies a somewhat strong Al–η^2-N_2 bonding. Therefore the cleavage of the corresponding N–N bond in the rearrangement of **A** to **17** is highly favored although no such bond dissociation energy data are available for comparison.[170]

Thus, the reaction of aluminum(I) monomer LAl with azobenzene has been investigated. The formation of a five-membered AlN_2C_2 ring (**17**) shows the difference in comparison with that of the [1 + 2] cycloaddition product by the reaction of LAl with alkyne, and indicates an interesting rearrangement of azobenzene via a possible three-membered AlN_2 intermediate (**A**) by interacting with LAl.

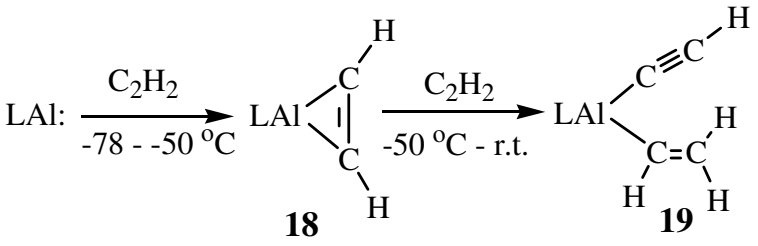
2.6. A Stable Aluminacyclopropene LAl(η^2-C_2H_2) and Its End-on Azide Insertion to an Aluminaazacyclobutene

*Abstract: A stable aluminacyclopropene LAl(η^2-C_2H_2) (**18**) has been isolated from the temperature controlled reaction of LAl with excess of C_2H_2. **18** further reacts with one molecule of C_2H_2 under ring opening and formation of terminal C≡CH and CH=CH_2 groups at aluminum to yield LAl(C≡CH)(CH=CH_2) (**19**). The reaction of LAl(η^2-C_2Ph_2) with one equiv of HCCPh smoothly afforded compound LAl(C≡CPh)[C(Ph)=CH(Ph)] (**20**). This reaction was further monitored by ^{1}H NMR spectral analysis, clearly disclosing the hydrogen migration of terminal HCCPh under the ring opening of Al(η^2-C_2). The end-on azide insertion in the Al(η^2-C_2) ring of **18** results in the first aluminaazabutene LAl[CH=CHN(N=NAr*)] (**21**).*

Heavier main group elements containing cyclopropenes have received considerable attentions due to their strained structure and remarkable reactivity. These compounds are often involved in reactions such as ring-opening, insertion, substitution, dimerization, and [1,2]-hydrogen migration,[171] and therefore are of great interest in syntheses, especially in the preparation of main group elements containing larger heterocycles with C–C unsaturated bonds.

These three-membered ring compounds with organic substituents at the two olefinic carbon atoms have been known.[155,160,171-175] However species with the simplest M(η^2-C_2H_2) moiety are either discussed on the basis of theoretical calculations,[176-180] or observed in metal vapor deposition reactions at 12 K.[181] Et(solvent)Al(η^2-C_2Ph_2) (solvent: Et_2O, THF) and ClAl(η^2-C_2R_2) (R = Me, Et) were assumed as intermediates in the respective formation of 1,4-(dialumina)cyclohexadiene and (ClAl·RC≡CR)$_4$.[182-185] Subsequently the bulky *β*-diketiminato ligand L stabilizes the Al(η^2-$C_2R^1R^2$) (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$); R^1, R^2: $SiMe_3$, Ph) rings. Such compounds have been prepared by the reductive coupling reaction of $LAlI_2$ and potassium in the presence of $R^1C{\equiv}CR^2$.[155] Correspondingly,

XAl(η^2-C_2H_2) (X = H, Cl) are suggested by calculations, however, they are unstable, as indicated by IR and ESR data on matrix isolated species at low temperatures.[179-180] Herein, we show the reaction of the aluminum(I) monomer, LAl[95] with C_2H_2 in the range from low to room temperature, and the successful isolation of the first stable aluminacyclopropene LAl(η^2-C_2H_2) (**18**) and its subsequent reaction product LAl(C≡CH)(CH=CH_2) (**19**). The reaction of **18** with a large bulky organic azide leads to an unusual insertion product, an aluminaazacyclobutene LAl[CH=CHN(N=NAr*)] (**21**, Ar* = 2,6-Ar'$_2C_6H_3$, Ar' = 2,4,6-$Me_3C_6H_2$).



L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2C_6H_3$

Scheme 15

The reaction of LAl with excess of carefully dried C_2H_2 in toluene was initially carried out in the range from –78 ºC to room temperature. The instant color change of the solution from red to orange and then the slow change to almost colorless were clearly observed, and compound LAl(C≡CH)(CH=CH_2) (**19**) was formed. Obviously, the formation of **19** indicated that LAl reacted with two molecules of C_2H_2. When this reaction was controlled in the temperature range from –78 to –50 ºC, the red solution only changed to orange (this color change even occurred when this reaction was performed at ca. –100 ºC). By removal of unreacted C_2H_2, a 1:1 adduct LAl(η^2-C_2H_2) (**18**) was isolated (Scheme 15). It is noted that when this reaction was continued without removing excess of C_2H_2, the corresponding ^{1}H NMR spectrum has shown the formation of small amounts of **19**, whereas the reaction solution remained orange in color.

The formation of **18** essentially follows [1 + 2] cycloaddition with respect to the characters of LAl (one nonbonded electron pair at Al) and C_2H_2 (C≡C π electrons). The interaction between C_2 and Al, in view of the theoretical molecular collision mechanism, gives the two extreme types: C_2 center to Al (channel a), and one of the C atoms of C_2 to Al (channel b). The DFT calculations by analyzing the total potential energy of LAl plus C_2H_2 system versus Al···C distance show that channel a has an energy barrier (the most height at ca. 145 kJ/mol), while b has almost no barrier (Figure 10). Obviously, the reaction kinetically takes channel b, which means that reaction can occur almost without any energy supporting. This is in good agreement with our experimental observations. Moreover, the final calculations of the reaction energy of LAl and C_2H_2 to **18** (ca. 155 kJ/mol) imply a stronger Al–η^2-C_2H_2 bond in comparison to that of the disubstituted one (Al–η^2-$C_2R^1R^2$, ca. 88 kJ/mol).[155]

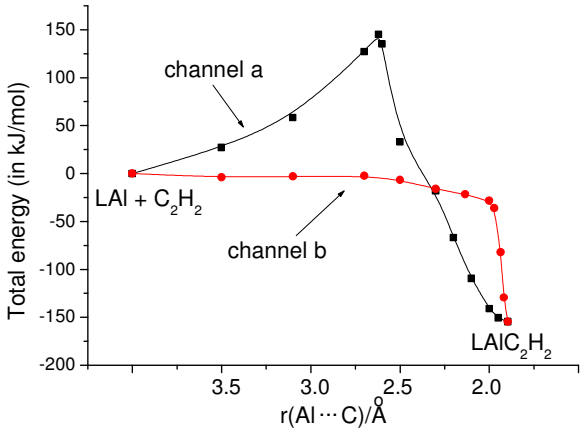
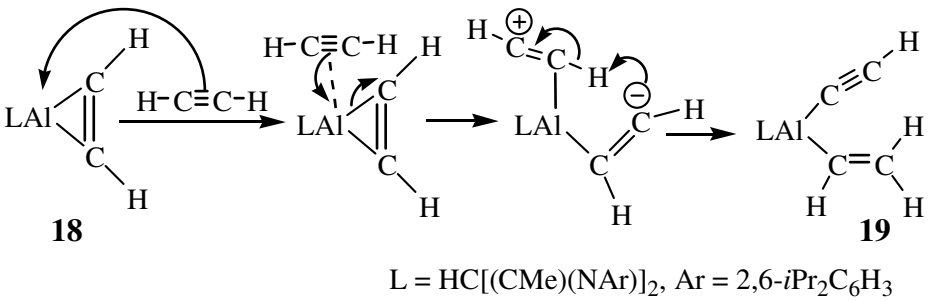


Figure 10. The total potential energy curve of LAl and C_2H_2 versus the Al···C distance.



L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Scheme 16

Further reaction of **18** with C_2H_2 may proceed through a donor-acceptor intermediate due to the Lewis acidic Al center of **18**. This mechanism has been extensively discussed in the

reaction of alkylaluminum(III) or alkylaluminum hydride compounds with alkynes,[4] and further evidenced by some experimental data.[186-188] The ring opening of Al(η^2-C_2) may occur with concomitant hydrogen migration from the π-coordinated C_2H_2 to result in **19** (Scheme 16). The latter ^{1}H NMR monitored reaction of LAl(η^2-C_2Ph_2) with a little excess of HCCPh to compound LAl(C≡CPh)[C(Ph)=CH(Ph)] (**20**) may clearly give a similar insight into this process.

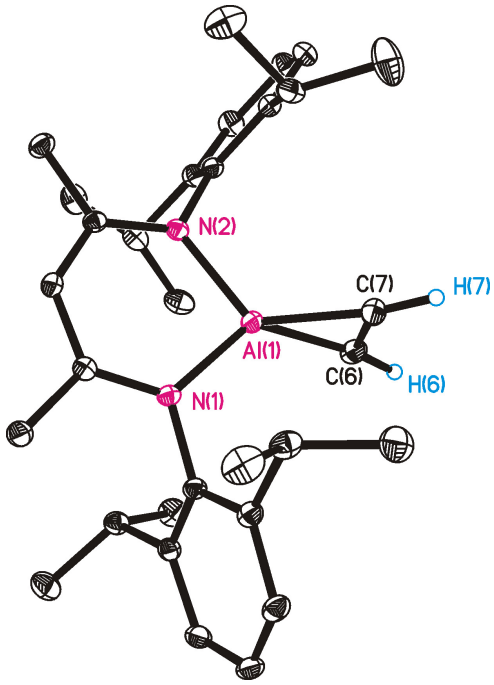


Figure 12. Molecular structure of **18**. H atoms in L are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.875(1), Al(1)–N(2) 1.884(1), Al(1)–C(6) 1.885(2), Al(1)–C(7) 1.878(2), C(6)–C(7) 1.358(2), C(6)–H(6) 1.000, C(7)–H(7) 1.021, N(1)–Al(1)–N(2) 97.98(5), C(6)–Al(1)–C(7) 42.30(7), Al(1)–C(6)–C(7) 68.57(10), Al(1)–C(7)–C(6) 69.13(10), H(6)–C(6)–C(7) 126.4, H(7)–C(7)–C(6) 127.1.

Compound **18** was obtained as an orange crystalline solid in quantitative yield. **18** is extremely air-sensitive. Its solution, once exposed to air, immediately changes its orange color to colorless. However, it is stable in an inert gas atmosphere. **18** is readily soluble in aromatic solvents and sparingly soluble in *n*-hydrocarbons. Compound **19** is a colorless crystalline

solid and is well soluble in hydrocarbons. **18** and **19** were characterized by mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and by X-ray crystallography.

The structural analyses clearly reveal that compound **18** has a three-membered Al(η^2-C_2H_2) ring (Figure 11), while **19** contains terminal C≡CH and CH=CH_2 groups at the Al atom (Figure 12). The latter is the first crystallographic authenticated example with terminal C≡CH and CH=CH_2 groups at the same Al atom. In **19**, the X-ray reflection data indicate that both C≡CH and CH=CH_2 groups are disordered in two positions (C(6)H(6)C(7)H(7)H(8), C(8)C(9)H(9), 62.2%; C(6A)H(6A)C(7A)H(7A)H(8A), C(8A)C(9A)H(9A), 37.8%). Thus, the central Al atom appears in a disordered tetrahedral geometry with N–Al–N bond angle of

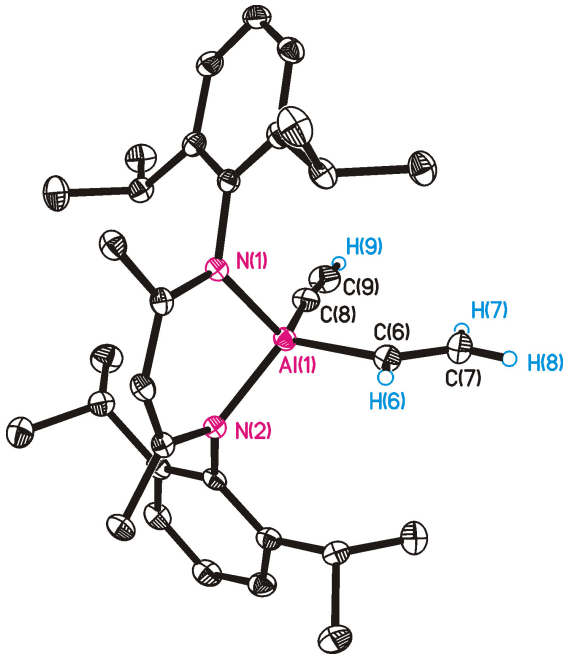


Figure 13. Molecular structure of **19**, the C≡CH and CH=CH_2 groups both in 62.2% occupation. H atoms in L are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.910(2), Al(1)–N(2) 1.895(1), Al(1)–C(6) 1.944(11), Al(1)–C(8) 1.962(11), C(6)–C(7) 1.325(17), C(8)–C(9) 1.173(11), N(1)–Al(1)–N(2) 96.99(6), C(6)–Al(1)–C(8) 110.8(4), Al(1)–C(6)–C(7) 124.6(12), Al(1)–C(8)–C(9) 173.9(13).

96.99(6)° and C–Al–C angles of 111.6(5)° (av). The Al–N bond lengths in **18** (1.875(1), 1.884(1) Å) are close to those in **19** (1.895(1), 1.910(2) Å), and are comparable to those

observed in compounds with four coordinate *β*-diketiminato aluminum(III) (1.888(2)-1.935(2) Å). However, they are shorter, in contrast to the longer Al–N bonds in LAl (1.957(2) Å) due to the larger radius of the Al(I)[95] compared to that of Al(III).

In **19**, the Al–C bond lengths (Al–$C_{C\equiv C}$, 1.941(14) Å (av); Al–$C_{C=C}$, 1.954(14) Å (av)) are comparable to those in related compounds $LAlMe_2$ (1.955(4)–1.961(3) Å) and L'$AlMe_2$ (L' = $HC[(CMe)(N–p\text{-tol})]_2$, 1.958(3)–1.970(3) Å). The C≡C (1.170(14) Å (av)) and C=C bond distances (1.323(18) Å (av)) are indicative of characteristic C–C triple and double bonds, while the Al–C≡C (175.4(19)º (av)) and Al–C=C (124.6(14)º (av)) angles deviate from the ideal 180º and 120º, respectively.[189] The ^1H and ^{13}C NMR spectra of **19** confirm the functional $CH=CH_2$ and C≡CH groups at Al. In $CH=CH_2$, the corresponding protons resonate at *δ* 5.70–6.20 ppm and carbons at *δ* 125.4 (=*C*H_2) and 138.0 (br, Al–*C*H=) ppm, respectively, and are within the typical alkenyl range. Three groups of double doublets are indicative for three non-equivalent protons. While the latter exhibits the proton resonance at *δ* 1.55 (s) ppm and carbon resonances at *δ* 94.6 (br, ≡CH) and 137.3 (br, Al–C≡) ppm. The absorptions at 1996 and 3270 cm^{-1} in the IR spectrum of **19** are tentatively assigned to the stretching frequencies of C≡C and ≡C–H bonds.

In **18**, the parameters within Al(η^2-C_2H_2) moiety (Al–C 1.882(2) Å (av), C–C 1.358(2) Å, C–H 1.010 Å (av); C–Al–C 42.30(7)º, Al–C–C 68.85(10)º (av), H–C–C, 126.6º (av)) fit well when compared with those of Al(η^2-C_2) in LAl(η^2-$C_2R^1R^2$) (R^1, R^2: $SiMe_3$, Ph) (Al–C 1.889(2)–1.899(3) Å, C–C 1.356(5)–1.382(4) Å; C–Al–C 42.02(14)–42.57(11)º, Al–C–C 68.39(15)–68.80(19)º),[155] and are also much closer to those in the calculated HAl(η^2-C_2H_2) (Al–C 1.844–1.852 Å, C–C 1.362–1.384 Å, C–H 1.076–1.089 Å; H–C–C, 126.8–127.3º).[179] It is noteworthy that in the Al(η^2-C_2H_2) ring of **18** the average Al–C and C–C bond lengths are respectively shorter and longer than those in **19** (deviation of 0.072 and 0.036 Å). This may indicate a conjugated ring system in Al(η^2-C_2). Furthermore, the ^1H and ^{13}C NMR spectra recorded in C_6D_6 show the proton (*δ* 8.82 (s) ppm) and carbon resonances (177.2 (br) ppm) of

the Al(η^2-C_2H_2) moiety in the low-field region characteristic for the alkenyl system. The results are indicative for a certain aromatic character of the Al(η^2-C_2) ring.

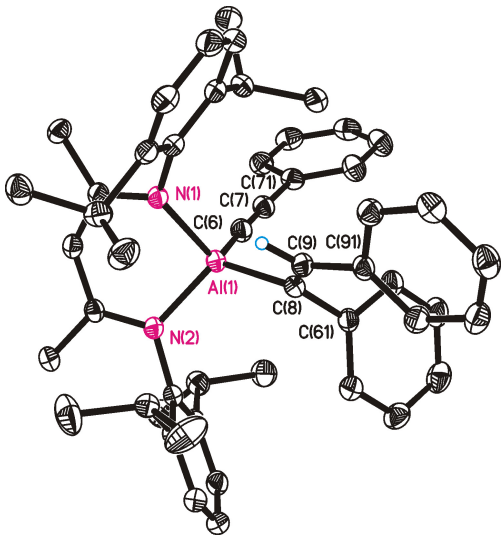


Figure 14. Molecular structure of **20**. Selected bond lengths (Å) and angles (º): Al(1)–N(1) 1.894(2), Al(1)–N(2) 1.895(2), Al(1)–C(6) 1.941(2), Al(1)–C(8) 1.971(2), C(6)–C(7) 1.217(2), C(8)–C(9) 1.343(3), N(1)–Al(1)–N(2) 97.04(6), C(6)–Al(1)–C(8) 111.15(8)

The reaction of LAl(η^2-C_2Ph_2) with one equiv of HCCPh smoothly afforded compound LAl(C≡CPh)[C(Ph)=CH(Ph)] (**20**). The molecular structure of **20** is presented in Figure 14.

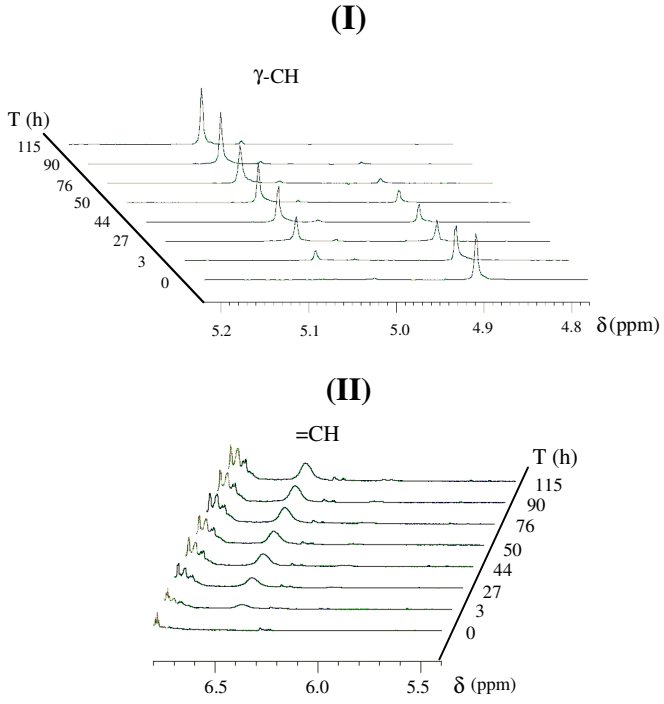
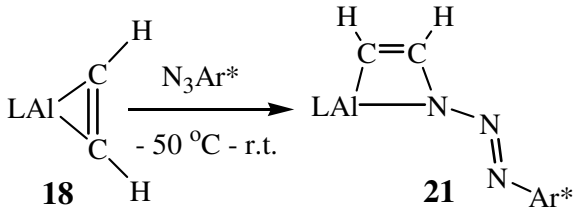


Figure 15. The ^{1}H NMR spectra monitored reaction of LAl(η^2-C_2Ph_2) with HCCPh

This reaction was further monitored by ^{1}H NMR spectral analysis (Figure 15). (I) clearly shows the gradual consumption of starting material LAl(η^2-C_2Ph_2) and formation of product **20** by the indication of γ-CH of LAl moiety with reaction time. (II) reflects the gradual generation of olefinic proton corresponding to AlC(Ph)=CH(Ph) moiety, indicating the hydrogen migration from HCCPh molecule.



L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$
Ar* = 2,6-Ar'$_2$C$_6$H$_3$, Ar' = 2,4,6-Me$_3$C$_6$H$_2$

Scheme 17

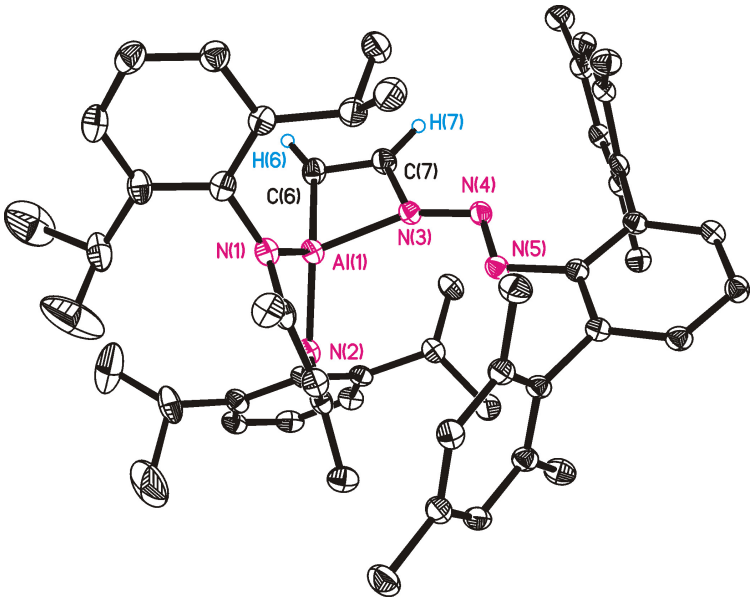


Figure 16. Molecular structure of **21**. H atoms in L are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.866(2), Al(1)–N(2) 1.867(2), Al(1)–N(3) 1.892(2), Al(1)–C(6) 1.932(3), C(6)–C(7) 1.342(4), C(7)–N(3) 1.410(3), N(3)–N(4) 1.320(3), N(4)–N(5) 1.284(3), N(1)–Al(1)–N(2) 99.8(1), C(6)–Al(1)–N(3) 72.6(1), Al(1)–N(3)–C(7) 88.2(2), Al(1)–C(6)–C(7) 88.5(2), C(6)–C(7)–N(3) 110.7(2), N(3)–N(4)–N(5) 112.4(2).

The reaction of **18** with a large bulky azide N_3Ar^* exhibits an unusual end-on azide insertion, resulting in a four-membered aluminaazacyclobutene **21** (Scheme 17). There are a handful of reactions known between monovalent organo-group 13 compounds and organic azides.[124,127,129-130,190-192] The initial N_2 elimination is generally accepted, and supported by the experimental observation. The formation of a five-membered AlN_4 ring in $LAl[(NSiMe_3)_2N_2]$ was suggested proceeding through a [2 + 3] cycloaddition of an Al=N intermediate and N_3SiMe_3. While the disubstituted aluminacyclopropene $LAl[(\eta^2\text{-}C_2(SiMe_3)_2]$ reacted under disassociation and N_2 elimination with a similar bulky azide to an Al=N compound.[155] Accordingly, the end-on N_3Ar^* insertion in the $Al(\eta^2\text{-}C_2)$ ring unambiguously reveals the initial interaction between an Al center and the end-on N atom of the azide group. This type of reaction is, to the best of our knowledge, so far unknown. Compound **21** has been well characterized by spectroscopic, analytical, and X-ray crystal measurements. The molecular structure of **21** is viewed in Figure 16.

In general, the first stable aluminacyclopropene $LAl(\eta^2\text{-}C_2H_2)$ (**18**) has been prepared by the direct reaction of LAl with C_2H_2 and structurally characterized. The crystallographic and NMR spectral data of **18** indicate a delocalized $Al(\eta^2\text{-}C_2)$ heterocycle, which can be described as a Hückel 2π aromatic system. The subsequent reaction of **18** with C_2H_2 to **19** shows its high reactivity. The end-on N_3Ar^* insertion in the $Al(\eta^2\text{-}C_2H_2)$ ring of **18** to the aluminaazacyclobutene **21** exhibits a novel reaction pattern of aluminacyclopropenes, and reflects the unusual trapping ability of **18**. Further investigation of the reactivity of **18** is underway.

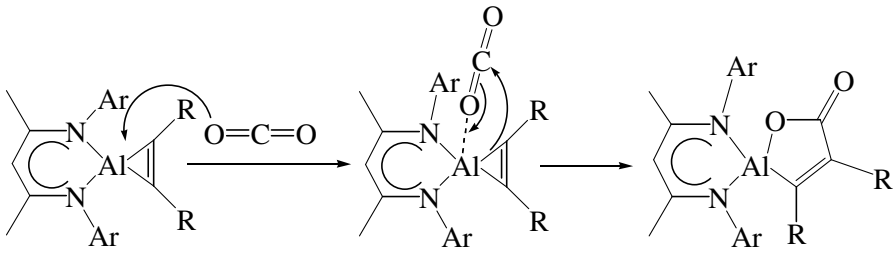
2.7. A Seven-membered Aluminum Allenyl Sulfur Heterocycle Arising from the Conversion of an Aluminacyclopropene with CS_2

*Abstract: The reaction of an aluminacyclopropene LAl[η^2-$C_2(SiMe_3)_2$] (L = $HC(CMeNAr)_2$, Ar = 2,6-$iPr_2C_6H_3$) with CS_2 in the temperature range from –78 ºC to room temperature affords the first seven-membered aluminum sulfur containing heterocyclic compound [LAl]$_2$(μ-S)[η^2-$SC(SiMe_3)$=C=$C(SiMe_3)$] (**24**) bearing an allenyl group. The structural characterization of **24** and the analogous compound LAl[$OC(O)C_2R_2$] (R = Ph (**22**), $SiMe_3$ (**23**)) of the proposed intermediate **A** and the variable-temperature ^{1}H NMR kinetic study of this reaction may give a better understanding on this unusual conversion.*

There is a widespread interest in main group heterocyclic compounds due to their applications in pharmaceutical, agrochemical, and material science.[154] In recent years, the number of group 13 metal heterocycles has increased. Within the heterocycles those containing multiple bonds have shown interesting structural features and properties. The $M^nN_2C_2$ (M = Al, Ga, In, n = 2; M = Ga, n = 1, 3)[193-198] and MC_3N_2 (M = Al, Ga)[95,199] heterocycles with C=C or C=N double bonds are exhibiting high electron density. The three-membered AlC_2 ring with a C=C bond shows a highly strained structure and good reactivity.[155] Nonetheless, such species are rare, and the heteroatoms within cycle are limited to C, N, and O elements due to the lack of appropriate synthetic routes. Herein we report on a seven-membered $Al_2C_3S_2$ heterocycle bearing a C=C=C allenyl group prepared from the reaction of an aluminacyclopropene, LAl[η^2-$C_2(SiMe_3)_2$] (L = $HC(CMeNAr)_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with carbon disulfide. Interestingly, the unusual formation of the allenyl group, to the best of our knowledge, is hitherto unknown in organoaluminum chemistry.

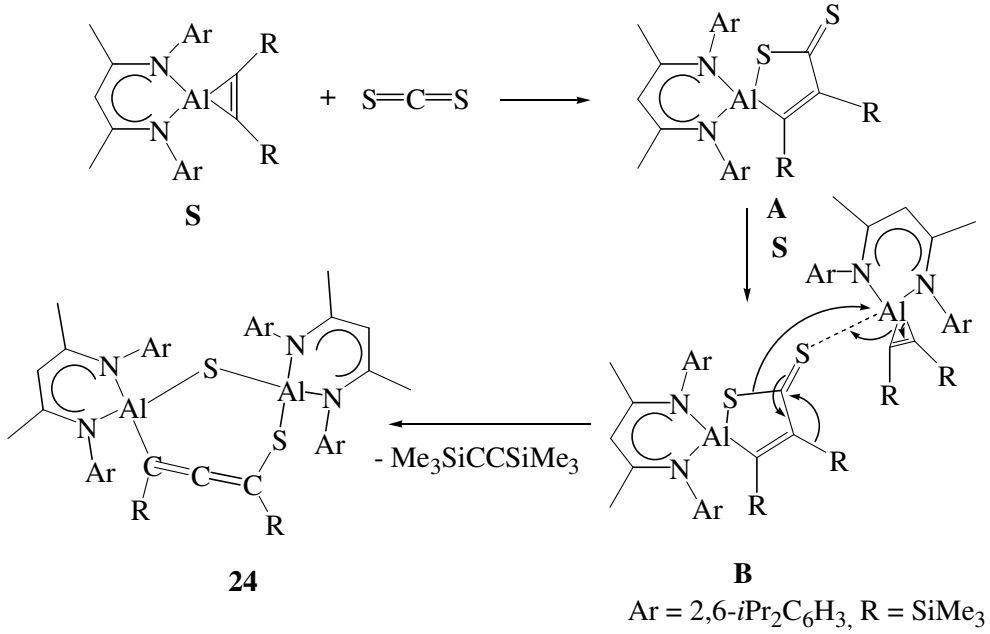
The addition of neat carbon disulfide to the solution of LAl[η^2-$C_2(SiMe_3)_2$] in toluene was carried out at –78 ˚C. In the course of warming the solution to room temperature, the color changed from red-black to green, to yellow green, and finally to yellow. An additional stirring for 12 h resulted in the formation of **24**.

The initial reaction of LAl[η^2-$C_2(SiMe_3)_2$] with CS_2 resembles closely to that of LAl[η^2-C_2R_2] (R = Ph, $SiMe_3$) with CO_2 (Scheme 18),[155] resulting in the generation of the five-membered heterocycle LAl[$SC(S)C_2(SiMe_3)_2$] (**A**). Obviously, **A** further interacts with a



Ar = 2,6-*i*$Pr_2C_6H_3$, R = Ph (**22**), $SiMe_3$ (**23**)

Scheme 18



S **A** **B** **24**

Ar = 2,6-*i*$Pr_2C_6H_3$, R = $SiMe_3$

Scheme 19

second molecule of LAl[η^2-$C_2(SiMe_3)_2$] at the donor exocyclic S atom in **A** and the acceptor Al center in LAl[η^2-$C_2(SiMe_3)_2$] to give intermediate (**B**). The fact whether one equivalent or excess of CS_2 was employed, only product **24** was isolated, indicates the stronger competitive reaction of **A** with LAl[η^2-$C_2(SiMe_3)_2$] than with CS_2. **B** reacts further under elimination of one molecule of $Me_3SiCCSiMe_3$ due to the weak Al–η^2-C_{alkyne} bonding (the bond dissociation energy of Al–η^2-C_2 is only 95.8 kJ/mol and therefore much less than that of Al–C_{methyl} in $AlMe_3$[4] ($D_{average}$, 281.4 kJ/mol). The free $Me_3SiCCSiMe_3$ is detected in the latter ^{1}H NMR

kinetic study. An easy migration of one Me_3Si group[200] and rearrangement of $C{=}S_{exo}$ and μ-S–C bonds lead to the unique formation of the thioallenyl functional group and the final product **24**. A proposed mechanism for the formation of **24** is given in Scheme 19. A parallel investigation of $LAl[\eta^2\text{-}C_2(SiMe_3)_2]$ with S_8 resulted in the formation of a dimer $[LAlS]_2$.. Evidently, the bulky β-diketiminato ligand with the steric and electronic stabilizing properties acts as an optimal skeleton for the aluminum center throughout the reaction process.

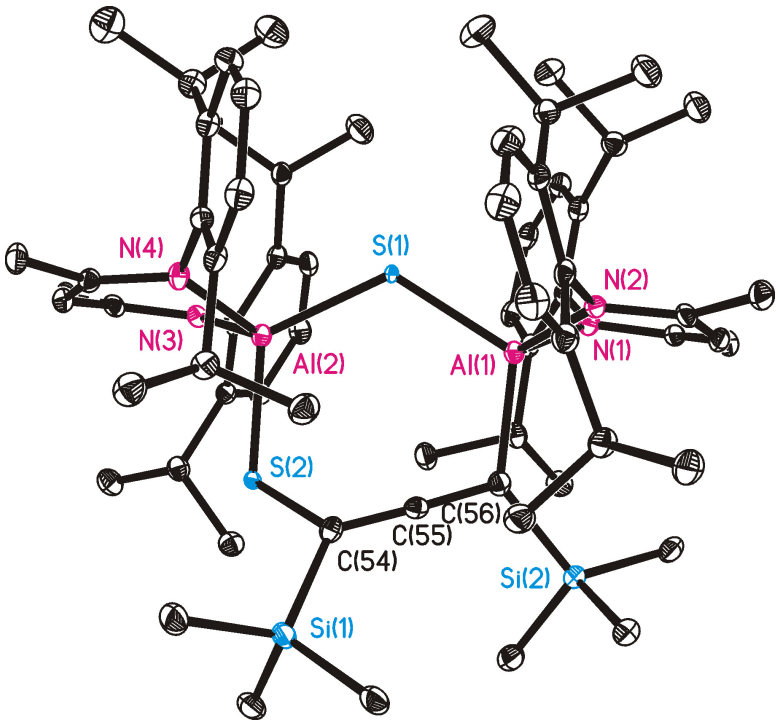


Figure 17. Molecular structure of **24** (without H atoms). Selected bond lengths (Å) and angles (°): Al(1)–S(1) 2.2298(11), Al(1)–C(56) 1.990(3), Al(2)–S(1) 2.2188(11), Al(2)–S(2) 2.2270(11), S(2)–C(54) 1.809(3), C(54)–C(55) 1.325(4), C(55)–C(56) 1.316(4); Al(1)–S(1)–Al(2) 122.57(4), C(54)–C(55)–C(56) 178.0(3).

Compound **24** was obtained as yellow crystals, which were characterized by spectroscopy and by X-ray crystallography. The structural analysis of **24** reveals a novel heterocyclic molecule (Figure 17), which is in sharp contrast to those of known dinuclear aluminum sulfides or thiolates. Each aluminum atom is chelated by a β-diketiminato ligand to form LAl moieties. Between the two LAl, one S atom and one $SC(SiMe_3)CC(SiMe_3)$ group are forming

each a bridge. The bond lengths of Al–S_{bridge} (2.2188(11), 2.2298(11) Å) and Al–$S_{thioallenyl}$ (2.2270(11) Å) are in the range (2.10–2.30 Å) of dinuclear aluminum sulfides. However, the bond angle of Al(1)–S(1)–Al(2) (122.57(4)º) is the widest among those of dinuclear aluminum sulfides or thiolates (78.1–117.5º).[201-202] The two central Al atoms, the μ-S atom and the SCCC group constitute one seven-membered $Al_2C_3S_2$ ring, of which S(2), Al(2), S(1), Al(1) and C(56) are arranged within a plane (mean deviation Δ = 0.0375 Å), while the C(56)C(55)C(54) group is located outside of this plane. The remarkable feature of **24** is the $SC(SiMe_3)CC(SiMe_3)$ group. The similar adjacent C–C bond distances (1.316(4), 1.325(4) Å) and the almost linear C–C–C angle (178.0(3)º) indicate the C=C=C allenyl functionality. A comparable example is only observed in *trans*-Rh[η-$C(CH{=}CH_2){=}C{=}CPh_2$](CO)(P-*i*$Pr_3)_2$] (1.308(6), 1.332(6) Å and 177.5(5)º).[203] The IR spectrum shows one weak band (1840 cm^{-1}) assignable to this bridged thioallenyl group. The deliberate ^{13}C NMR spectral studies give an unambiguous assignment of such allenyl (Al-$C(SiMe_3){=}C{=}C(SiMe_3)S$) carbon resonances ($\delta$ 212.70 (=*C*=); 80.60, broad (Al–*C*=); 59.94 ppm (=*C*–S)).

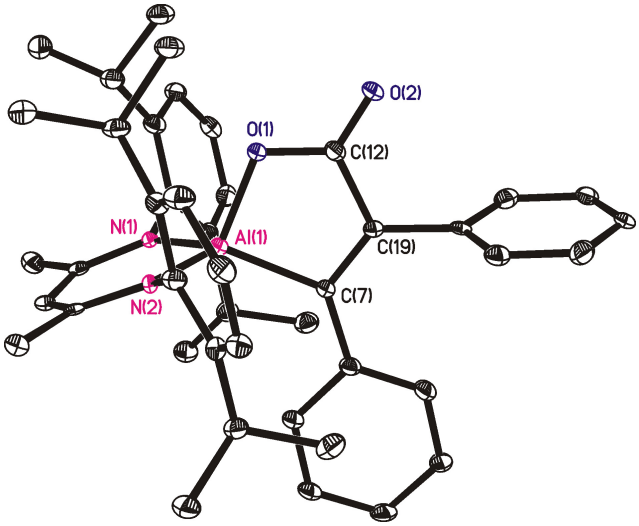


Figure 18. Molecular structure of **22** (without H atoms). Selected bond lengths (Å) and angles (˚): Al(1)–O(1) 1.776(3), Al(1)–C(7) 1.987(5), C(12)–O(1) 1.328(5), C(12)–O(2) 1.213(6), C(12)–C(19) 1.513(6), C(19)–C(7) 1.362(6); O(1)–C(12)–O(2) 122.5(4).

The crystal structure evidence of **22** and **23** may approach to that of **A** (Figures 18 and 19). As expected, the CO_2 was inserted into one of the Al–C bonds to form a five-membered AlC_3O planar ring with an *exo* C=O group (Δ = 0.0199 Å). The longer bond distances and weaker bond strength of CS_2 than those of the corresponding CO_2[204-205] might give rise to the further interaction of **A** with $LAl[\eta^2\text{-}C_2(SiMe_3)_2]$ and rearrangement of the $C{=}S_{exo}$ unit.

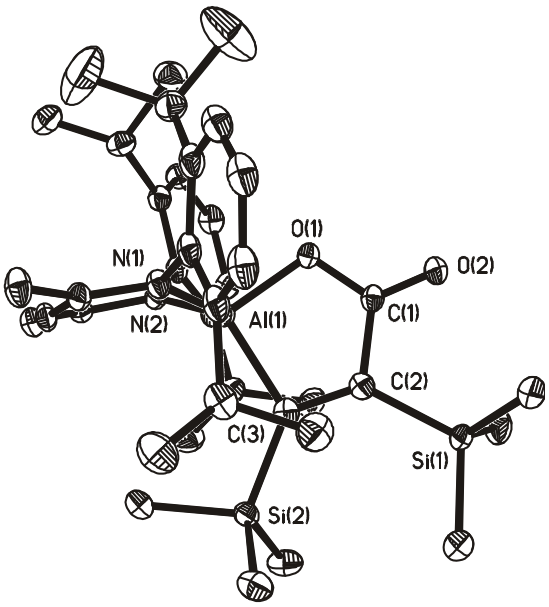


Figure 19. Molecular structure of **23** (without H atoms). Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.7696(12), Al(1)–C(3) 1.9891(17), C(1)–O(1) 1.331(2), C(1)–O(2) 1.218(2), C(1)–C(2) 1.530(2), C(2)–C(3) 1.364(2); O(1)–C(1)–O(2) 121.78(15).

The variable-temperature ^{1}H NMR spectroscopy regarding the reaction of $LAl[\eta^2\text{-}C_2(SiMe_3)_2]$ and excess of CS_2 in [D_8]toluene was monitored. The assignments of Ib, Ic, IIf and IIg were referenced to the ^{1}H NMR spectra of **24**. The assignment of free $Me_3SiCCSiMe_3$ (Id) was referenced to the ^{1}H NMR spectrum of the commercially available $Me_3SiCCSiMe_3$ in [D_8]toluene at room temperature (δ_{SiMe3} = 0.14 ppm). From -20 ºC to 80 ºC, that the gradual completion of (IIf) and (IIg) proceeds the coalescence to separation is temperature-dependant. The less than 1:1 integral intensity of **24** to the free $Me_3SiCCSiMe_3$ might be due to excess of CS_2, since traces of CS_2 are difficult to control in the ^{1}H NMR experiment.

This variable-temperature ^{1}H NMR kinetic study of this reaction (Figure 20) reveals the gradual consumption of LAl[η^2-$C_2(SiMe_3)_2$] (a) and formation of **24** (b and c) including the byproduct $Me_3SiCCSiMe_3$ (d) in (I). While in (II), this process is accompanied by the occurrence and quick disappearance of some resonances, indicating that this conversion proceeds via the proposed intermediates **A** and **B** to completion.

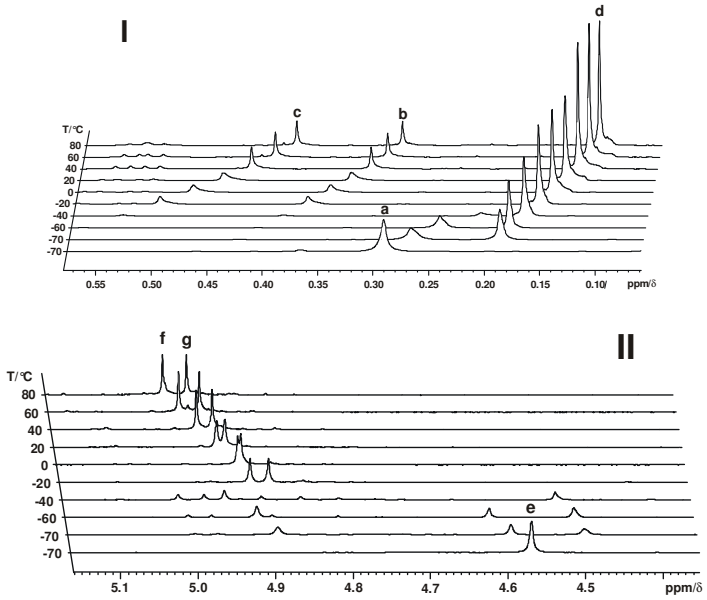


Figure 20. Variable-temperature ^{1}H NMR kinetic studies of the reaction of LAl[η^2-$C_2(SiMe_3)_2$] with excess CS_2 in [D_8]toluene. (I) records the resonances of $SiMe_3$ (0.10–0.55 ppm) which correlate with changes of η^2-$C_2(SiMe_3)_2$ group and (II) shows those of γ-CH protons (4.4–5.1 ppm) directly with the changes of LAl moieties (a and e correspond to LAl[η^2-$C_2(SiMe_3)_2$], b,c,f and g to **24**, d to free $Me_3SiCCSiMe_3$).

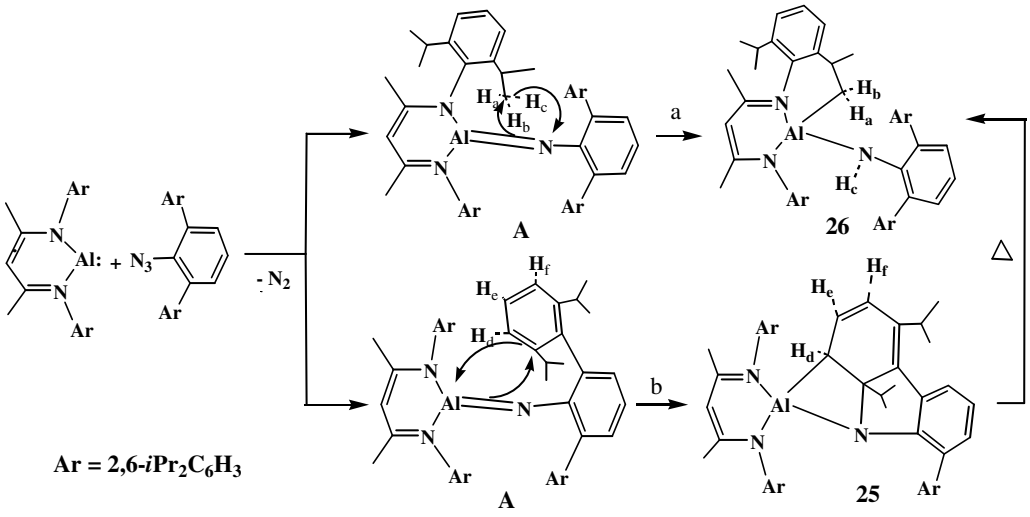
Thus, an unusual conversion of LAl[η^2-$C_2(SiMe_3)_2$] with CS_2 to **24** has been shown, where the search of sterically and energetically favored unsaturated substrate CS_2 is crucial. The investigation on such selenium or tellurium containing heterocycles is in progress.

2.8. Two Types of Intramolecular Addition of an Al=N Multiple Bonded Monomer LAl=NAr' Arised from the reaction of LAl with N_3Ar'

Abstract: The reaction of β-diketiminated aluminum(I) monomer LAl with a large bulky azide N_3Ar' (L = $HC(CMeNAr)_2$, Ar' = 2,6-$Ar_2C_6H_3$, Ar = 2,6-$iPr_2C_6H_3$ ***25*** *and* ***26****, which have been characterized by spectroscopic and X-ray structural analyses, as well as elemental analysis. The variable-temperature ^1H NMR kinetic studies of this reaction indicate the existence of the monomer LAlNAr' (****A****) at low temperature and the thermal stability of the compounds increases in the order of* ***A < 25 < 26.***

Considerable attention has been attracted to the heavier group 13 imides, since they can be used as single-source precursors for metal nitrides, which have interesting electronic properties and therefore important applications for technological materials.[206] In recent years, studies of the syntheses and characterization of such compounds have shown that they have a strong tendency to associate, even to oligomerize. However, the modification of the substituents on both metal and nitrogen of the $(MN)_n$ core have a great effect on their aggregation. The preparation of di- and tri-coordinate imido monomers Ar'MNL'' (M = Ga, In; Ar' = 2,6-$Ar_2C_6H_3$, Ar = 2,6-iPr$_2C_6H_3$, L'' = 2,6-(4-tBu-Xyl)$_2C_6H_3$) and LMNL' (M = Al, Ga; L = $HC[(CMe)(NAr)]_2$, L' = 2,6-$Trip_2C_6H_3$, Trip = 2,4,6-iPr$_3C_6H_2$), which have the lowest degree of association and the unique M–N multiple bond, demonstrates the stabilization of Al (Ga or In) imido monomers by the large bulky ligands.[191] Nonetheless, the syntheses of compounds containing a Ga_2N_2 or a AlN_4 ring,[129,190] which are proposed to proceed through the monomeric Al(Ga) imide, in the absence of steric protection, suggests the high reactivity of such monomers. Herein we show that the latent reactivity of a monomeric Al-N multiple bonded species initiates further intramolecular addition. The reaction of the *β*-diketiminated LAl with the bulky N_3Ar' can afford two different isomers **25** and **26** derived from their parent imide LAlNAr' (**A**). Also of great interest is the thermal conversion of **25** into **26**. This indicates the difference of the thermal stability between **25** and **26**.

The reaction of LAl with N_3Ar' was carried out at -78 ºC and allowed to warm to room temperature. Partial removal of toluene and addition of *n*-hexane led to crystallization of compounds **26** (colorless crystals in 24% yield) and **25** (yellowish crystals in 42% yield), one after the other. Crystals of **25** are of X-ray quality, while single crystals of **26** were obtained when **25** was treated by dissolving in a hot toluene/*n*-hexane mixture and then kept at 4 ºC to allow to crystallize. This suggests that a thermal conversion of **25** to **26** is occuring.



Scheme 20

The LAl reacting with N_3Ar' may proceed through an intermediate LAlNAr' (**A**) with elimination of N_2. A similar reaction of LM (M = Al, Ga) with N_3L' has been reported to afford LMNL' containing a M=N multiple bond.[191] The latter ^{1}H NMR kinetic study also suggests the existence of **A** at low temperature. Compound **25** is formed as a result of a [2 + 2] cycloaddition of a phenyl ring of the Ar' substituent on nitrogen (route b, Scheme 20), while the formation of **26** might occur by an intramolecular C–H activated addition involving the methyl group of the isopropyl substituent on the *β*-diketiminato ligand (route a).

Compounds **25** and **26** are thermally stable. They change with color at ~320 ºC and finally melt at 381–382 ºC. Both of them show the molecular ion [M^+ - 1] at m/z 855. They have been characterized by spectroscopic, analytical and X-ray crystal measurements.

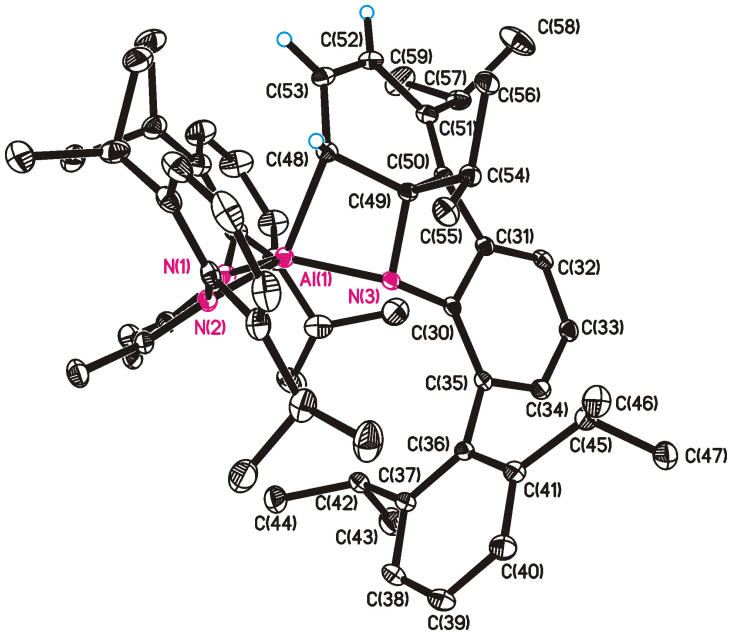


Figure 21. Molecular structure of **25**. Selected bond lengths (Å) and angles (°):Al(1)–N(1) 1.915(2), Al(1)–N(2) 1.926(2), Al(1)–N(3) 1.876(2), Al(1)–C(48) 1.998(3), C(48)–C(49) 1.536(4), C(49)–C(50) 1.520(4), C(50)–C(51) 1.348(4), C(51)–C(52) 1.469(4), C(52)–C(53) 1.336(4), C(53)–C(48) 1.475(4), N(3)–C(49) 1.537(3), N(1)–Al(1)–N(2) 96.92(10), N(3)–Al(1)–N(1) 127.76(10), N(3)–Al(1)–N(2) 117.99(10), N(3)–Al(1)–C(48) 78.53(10), Al(1)–N(3)–C(30) 138.71(17).

The structure of **25** (Figure 21) exhibits a [2 + 2] cycloaddition product. The four-membered $AlNC_2$ ring is quasi-planar (Δ = 0.0680 Å) with Al–N bond length (1.876(2) Å) longer than those in the AlN_4 ring complex (1.851(2), 1.8152(15) Å)[127] and Al–C distance (1.998(3) Å) similar to that in the AlC_3O ring compound (1.9852(16) Å).[155] The phenyl ring involved in the [2 + 2] cycloaddition becomes non-planar, where C(50), C(51), C(52) and C(53) are in plane (Δ = 0.0430 Å), C(48) and C(49) are away from this plane by 0.1813 and –0.2827 Å. The C–C bond lengths for C(50)–C(51) and C(52)–C(53) are 1.348(4) and 1.336(4) Å and are typical of C=C double bonds,[207] while the remaining four C–C distances are in the range (1.469(4)–1.536(4) Å) and are indicative for C–C single bonds. The structural features of this phenyl ring are in good agreement with the proton NMR spectrum. The resonances at δ

6.08 (dd), 5.41 (d), and 2.43 (d) ppm are assigned to H_e, H_f and H_d, respectively, reflecting the extent of (un)saturation at the carbons where these protons are attached.

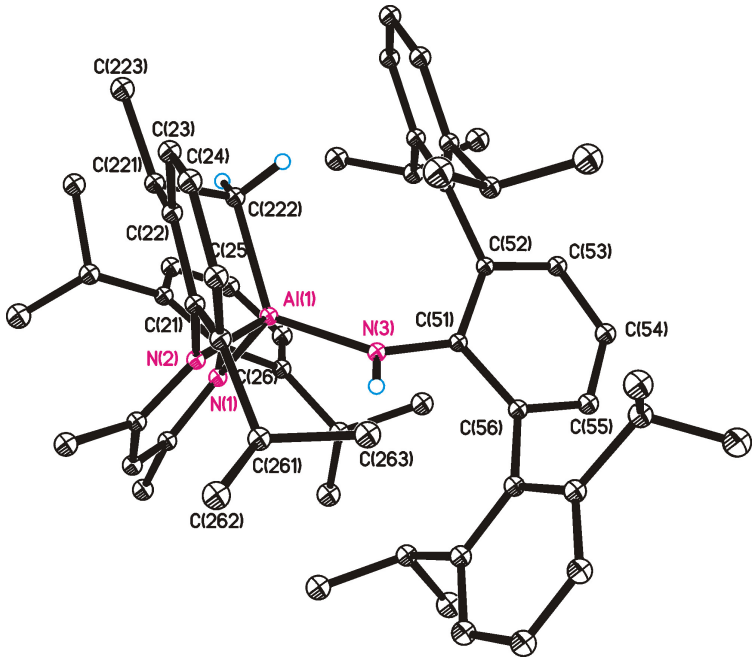


Figure 22. Molecular structure of **26**. Selected bond lengths (Å) and angles (˚): Al(1)–N(1) 1.940(2), Al(1)–N(2) 1.913(2), Al(1)–N(3) 1.858(2), Al(1)–C(222) 1.961(3), C(222)–C(221) 1.556(3), N(1)–Al(1)–N(2) 95.69(10), N(3)–Al(1)–N(1) 115.78(9), N(3)–Al(1)–N(2) 103.44(10), N(3)–Al(1)–C(222) 122.34(10), Al(1)–N(3)–C(51) 138.72(16)

The X-ray crystal structure of **26** is shown in Figure 22. Compound **26** is monomeric and contains a tetra-coordinate Al (3N, 1C) center. The Al atom is involved as part of two fused six-membered rings (AlN_2C_3 and $AlNC_4$). The Al(1)–C(222) (1.961(3) Å) and C(222)–C(221) (1.556(3) Å) bond lengths are consistent with experimental values observed for Al–C and C–C single bonds. This suggests the absence of strain within the $AlNC_4$ ring formed as a result of Al–C ligation. The Al–NH(Ar') bond length (1.858(2) Å) falls within the range (1.75–1.85 Å) of terminal Al–N single bonds and a little shorter than that of Al(1)–N(3) in **25**. The NH and the CH_2 protons (H_a and H_b) resonate at δ 3.41 (s), –0.28 (dd) and –1.75 (t), respectively. The assignment of these Al–CH_2 (H_a and H_b) protons in the ^{1}H NMR spectrum of **26** is viewed in the following figure 23. The different dihedral angles between H(22B)–C(222)–

C(221)–H(22A) and H(22C)–C(222)–C(221)–H(22A) give rise to different coupling constants as $^{3}J_{H(22B)H(22A)}$ = 13.8 Hz and $^{3}J_{H(22C)H(22A)}$ = 3.0 Hz according to the Karplus formula of $^{3}J_{HH}$ = A – B•cosϕ + C•cos2ϕ (A = 7, B = –1, C = 5),[208] While $^{2}J_{H(22B)H(22C)}$ = –13.8 Hz, therefore, the resonances at δ –0.28 (dd) and –1.75 (t) are assigned to H(22B) (H_b) and H(22C) (H_a), respectively. The characteristic absorption at 3298 cm^{-1} is assignable to ν_{NH} in the IR spectrum of **26**.

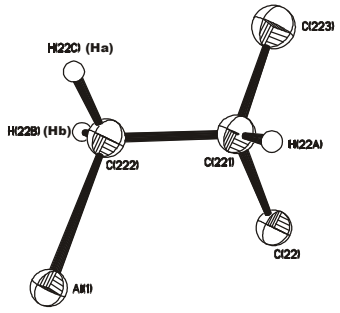


Figure 23

Now we gain further insight into the reaction process between LAl and N_3Ar' carried out by a variable-temperature ^{1}H NMR study (Figure 24). To a mixture of equivalent LAl and N_3Ar' at –78 ˚C, pre-cooled D_8-toluene was added. At –70 ˚C, the proton NMR spectrum only presents the features indicated for those of N_3Ar'. This shows the only dissolving of N_3Ar' in D_8-toluene at this temperature. From –50 to –10 ˚C, the occurrence of a singlet at δ 5.05–4.60 ppm assigned for that of γ-CH proton in L indicates the starting and proceeding of this reaction, which initiate the dissolving of LAl species. The changes of the chemical shift of this singlet in this area are temperature-dependent. The sample was kept at 50 ˚C for 1 h and the corresponding proton NMR spectrum showed that there were no remarkable changes of resonances compared to those in the previous one at 50 ˚C. While for 24 h the measurement on the sample showed the great changes of resonances in the spectrum.

Therefore, the γ-CH of the starting material LAl resonates at ~5.10 ppm (the low temperature ^{1}H NMR spectrum of the starting material LAl was measured as a reference. The resonances of γ-CH at δ 5.11, 5.13, 5.14, and 5.15 ppm correspond at –50, –30 , –10, 25 ºC),

its change is a good indicator for the progress of the reaction. Thus in I, from –50 to –10 ºC, the occurrence of one singlet may indicate the formation of **A**. From –10 to 50 ºC, this singlet was gradually transformed into two other singlets, suggesting the further reaction of **A** and the

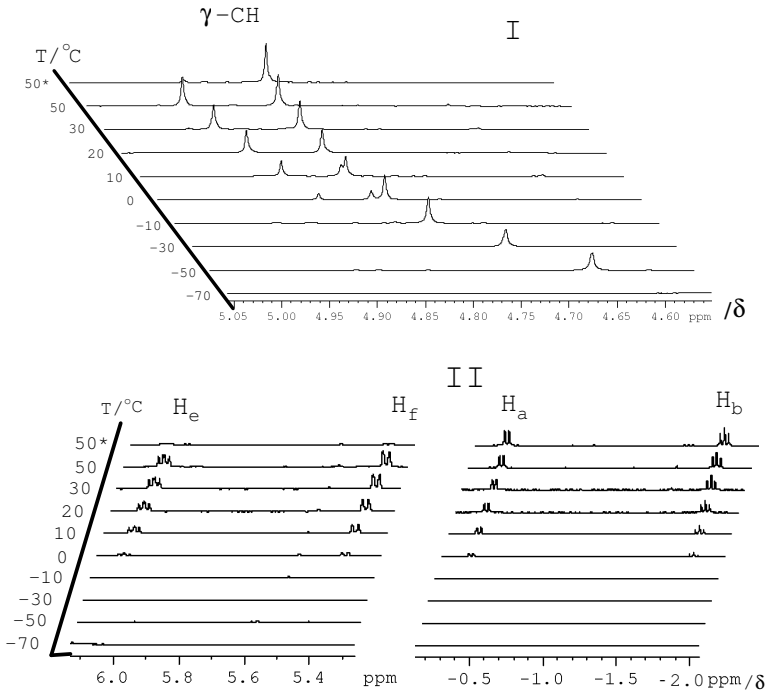


Figure 24. Variable-temperature ^{1}H NMR kinetic studies of the reaction of LAl with N_3Ar' in [D_8]toluene. (I) records the resonances of γ-CH proton (δ 5.05–4.60 ppm) which correlate with changes of LAl moiety and (II) shows those of **25** (H_f and H_g, δ 6.20–5.20 ppm) and **26** (H_a and H_b, δ 0.00– –2.00 ppm). 50* means the available ^{1}H NMR data by keeping the sample at 50 ºC for 24 h.

concomitant formation of compounds **25** and **26**. This is further evidenced by the corresponding presence of the characteristic proton resonances in II indicative for **25** and **26**, respectively. The almost same integral intensity of **25** and **26** shows the equiponderance of the intramolecular addition of **A** via routes a and b. Keeping this reaction at 50 ºC for 24 h, the final spectrum shows the disappearance of the characteristic resonances for **25** and the growing in of those for **26**. This experiment confirms the result of recrystallization of **25** from a hot solution to yield **26**.

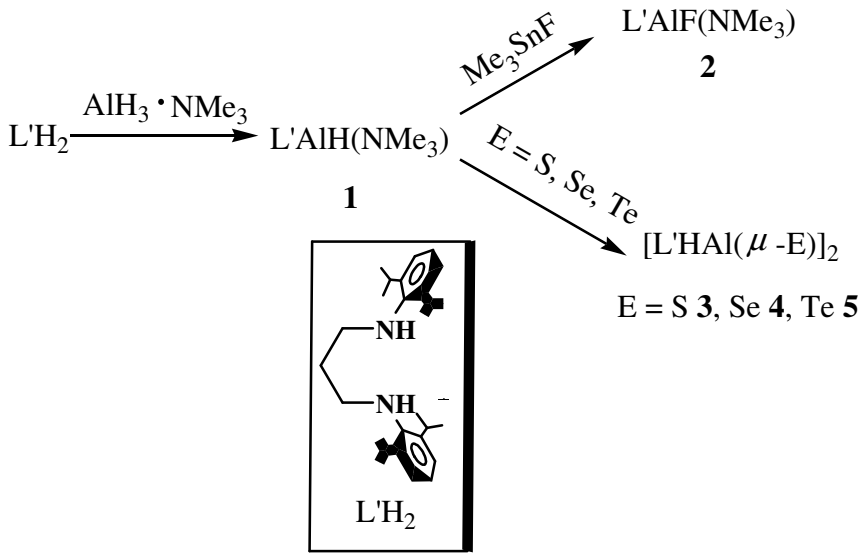
The strained structure of **25** (torsional AlC_2N and C_6 rings) compared to that of **26** may energetically favor this thermal rearrangement. While the deliberate ^1H NMR kinetic studies of this reaction unambiguously reveal the thermal stability of these three isomers in the order of **A < 25 < 26**.

At last, an unprecedented reaction, which occurs by an intramolecular addition to an Al–N multiple bonded species LAlNAr' and furthermore by rearrangement of **25** to **26** without changing the monomeric nature of the products, has been shown. Presently we are involved in the low temperature synthesis of **A** and especially its X-ray structural analysis.

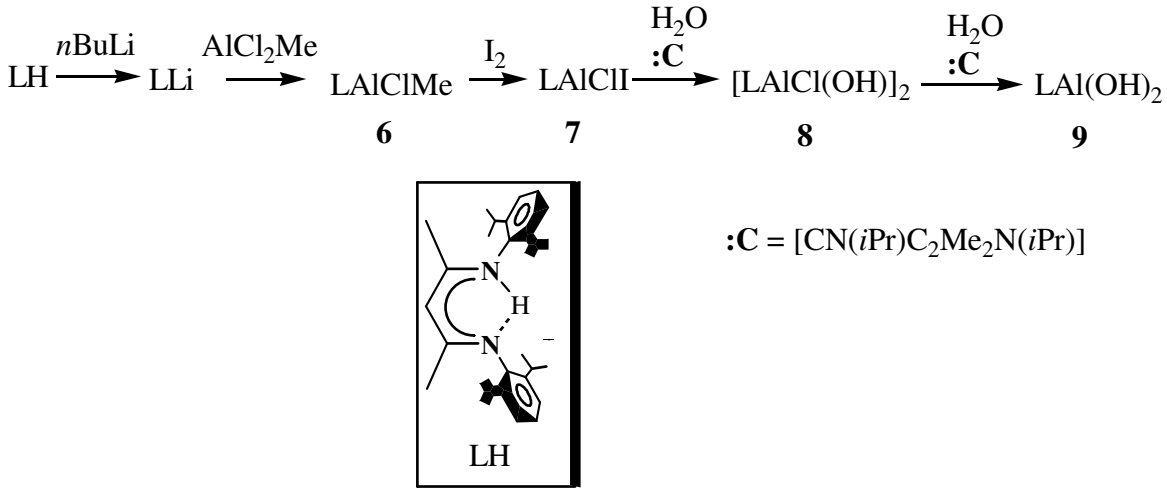
3. Summary and Outlook

In this thesis, the sterically bulky diamido L' and *β*-diketiminato L ligands are employed as supporting moieties in aluminum compounds. Compounds **1**–**26** have been isolated and characterized (Schemes 21, 22, and 23). The experimental results demonstrate that a number of functional reactions involving an Al(I) or Al(III) center are realized exhibiting diverse reaction types and rich organoaluminum chemistry.

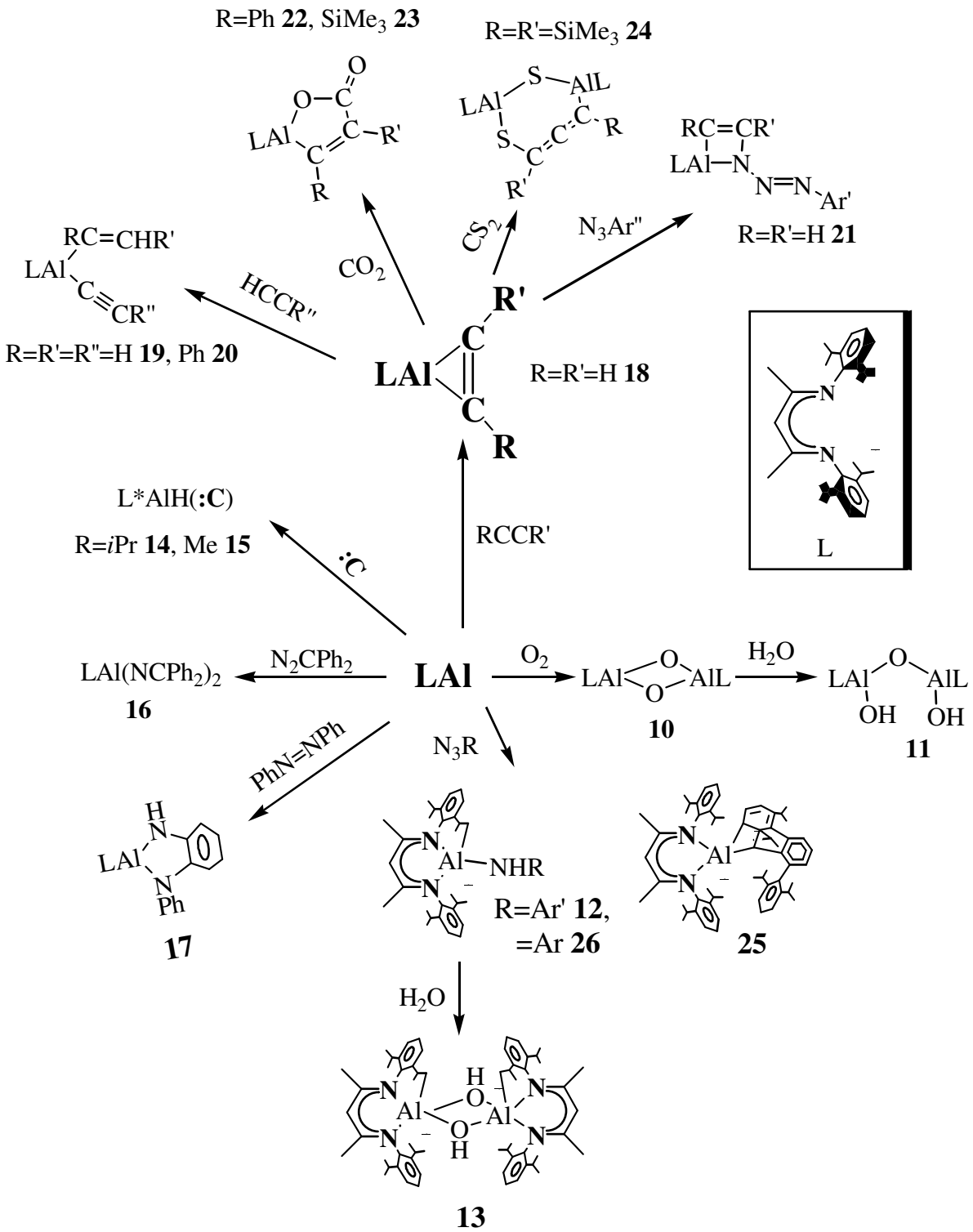
Moreover, organoaluminum chemistry has emerged as a more and more relatively mature field: new syntheses are being developed, much of its basic chemistry is being explored, and many of the prevailing structural types are in delineation. The motivating force for such fundamental studies has been the widespread industrial importance of these organometallic compounds in stoichiometric and catalytic processes.



Scheme 21



Scheme 22


R=Ph 22, SiMe3 23
R=R'=SiMe3 24
RC=CR'
LAl–N
N=N
Ar'
R=R'=H 21
RC=CHR'
LAl
CR"
R=R'=R"=H 19, Ph 20
HCCR"
CO2
CS2
N3Ar"
R'
LAl
R
R=R'=H 18
L
L*AlH(:C)
R=iPr 14, Me 15
:C
RCCR'
LAl(NCPh2)2
16
N2CPh2
LAl
O2
LAl
AlL
10
H2O
LAl
AlL
OH
OH
11
PhN=NPh
N3R
LAl
H
N
Ph
17
Al
NHR
R=Ar' 12,
=Ar 26
Al
25
H2O
Al
O
H
H
Al
13

Scheme 23

4. Experimental Sections

4.1. General Procedures

All manipulations were carried out under a dry nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glovebox filled with nitrogen, where the O_2 and H_2O level were strictly maintained below 1 ppm. All solvents were distilled from Na/benzophenone ketyl prior to use.

4.2. Physical measurements.

The melting points of all compounds described in this thesis were measured in sealed glass tubes on a Bühler SPA-1 apparatus and are not corrected.

Mass spectra were obtained on a Finnigan MAT 8230 or a Varian MAT CH5 instrument by EI-, FI-, and FAB-MS techniques.

IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer as Nujol mulls on KBr plates. Intensities were abbreviated as follows: s (strong), m (middle), w (weak). In most cases only the characteristic absorptions are listed.

^{1}H, ^{13}C, ^{19}F, ^{27}Al, ^{29}Si, and ^{77}Se NMR spectra were recorded on a Bruker-Avance-500, Avance-200, MSL-400, AM-250, and AM-200 spectrometers. The chemical shifts are reported in ppm (positive shifts being downfield) with reference to external standards ($SiMe_4$ for ^{1}H, ^{13}C, and ^{29}Si, $CFCl_3$ for ^{19}F, $AlCl_3$ for ^{27}Al, and Me_2Se for ^{77}Se nuclei). If not otherwise stated, the operation temperature was at ca. 298 K. The symbols (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, dd = double doublet, m = mutiplet) are used.

Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

X-ray structure determinations and refinements. The crystallographic data for **1**, **2**, **4**, **16,** and **17** were collected on a Stoe AED2, for **7, 8, 14, 18, 19, 20, 21, 25,** and **26** on IPDS II-

array detector system with four-circle instrument using graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å), and for **10, 12, 13, 22, 23,** and **24** on a bruker three-circle diffractmeter equipped with a SMART 6000 CCD detector using monochromated Cu-Kα radiation (λ = 1.54178 Å). All structures were solved by direct methods (SHELXS-97)[212] and refined with all data by full-least-squares against F^2.[213] The non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically. The hydrogen atoms were included in geometrically idealized positions with the *U*iso tied to that of the parent atoms and were refined with the riding model, or by difference Fourier synthesis and refined isotropically. Crystal data, data collection details, structural solution and refinement procedures for all the compounds are summarized in the tables.

4.3. Starting materials

Commercially available chemicals were purchased from Fluka or Aldrich and used as received. The gas phase chemicals such as O_2, HCCH, CO_2, CO, H_2CCH_2 are predried by P_4O_{10} perior to use. The other compounds used in the syntheses were prepared according to published references: L' (L' = $ArNH(CH_2)_3HNAr$, Ar = 2,6-*i*$Pr_2C_6H_3$),[31] $AlH_3{\cdot}NMe_3$,[209] Me_3SnF,[210] $[ArN(CH_2)_3NAr]AlMe$,[35] L (L = $HC[(CMe)(NAr)]_2$),[81] $LAlI_2$,[95] $[CN(R)C_2Me_2N(R)]$ (**:C**, R = Me, *i*Pr),[132] N_2CPh_2,[133] N_3R (R = Ar, Ar').[211]

4.4. Syntheses

[ArN(CH$_2$)$_3$NAr]AlH(NMe$_3$) (1)

A solution of diamine ArNH(CH$_2$)$_3$HNAr (4.03 g, 10.24 mmol) (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) in toluene (20 mL) was added to a solution of AlH$_3$·NMe$_3$ (1.18 g, 13.24 mmol) in toluene (30 mL). While stirring, gas evolution was observed. The mixture was slowly heated to 80 °C and stirred for 5 h. All volatiles were removed in vacuum and the residue was extracted with *n*-hexane. Filtered through Celite, the extract was evaporated to dryness to afford [ArN(CH$_2$)$_3$NAr]AlH(NMe$_3$) as a white solid. X-ray quality crystals were grown from *n*-hexane.

Yield: 4.41 g, 90%. M.p. 196–197 ºC.

^{1}H NMR (200.13 MHz, 300 K, C$_6$D$_6$, ppm): δ = 1.22, 1.37, 1.47, 1.66 (d, 24H, CH*Me$_2$*), 1.66 (s, 9H, N*Me$_3$*), 2.10, 3.00 (m, 2H, NCH$_2$C*H$_2$*), 3.25–3.45 (m, 4H, NC*H$_2$*), 3.63, 4.25 (sept, 4H, C*H*Me$_2$), 7.10–7.16 (m, 6H, Ar–*H*).

MS (EI): *m*/*z* = 420 [M^+ – NMe$_3$].

IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1799 (sh, Al–H).

C$_{33}$H$_{57}$AlN$_3$ (522.02) (**1**·1/2*n*-hexane): calcd. C 75.93, H 11.00, N 8.05; found C 75.44, H 10.64, N 8.26.

[ArN(CH$_2$)$_3$NAr]AlF(NMe$_3$) (2)

Method 1: A suspension of **1** (1.44 g, 3 mmol) and Me$_3$SnF (0.55 g, 3 mmol) in toluene (30 mL) was heated to 80 ºC and stirred for 12 h. After filtration, the filtrate was concentrated to ca. 10 mL in vacuum and kept at 4 ºC for 48 h to afford colorless block-shaped crystals of **2**.

Yield: 1.20 g, 80%. M.p. 220-222 ºC.

^{1}H NMR (200.13 MHz, 300 K, C$_6$D$_6$, ppm): δ = 1.22, 1.35, 1.47, 1.71 (d, 24H, CH*Me$_2$*), 1.75 (s, 9H, N*Me$_3$*), 2.00, 3.00 (m, 2H, NCH$_2$C*H$_2$*), 3.27, 3.40 (m, 4H, NC*H$_2$*), 3.64, 4.29 (sept, 4H, C*H*Me$_2$), 7.10–7.32 (m, 6H, Ar–*H*).

^{19}F NMR (188.29 MHz, 300 K, C$_6$D$_6$, ppm): δ = –12.4 (adjusted value, –175.4).

MS (EI): *m*/*z* = 497 [M^+], 438 [M^+ – NMe$_3$].

C$_{30}$H$_{49}$AlFN$_3$ (497.72): calcd. C 72.40, H 9.92, N 8.44; found: C 72.31, H 9.71, N 8.28.

Method 2: A suspension of **1** (1.44 g, 3 mmol) and Me$_3$SnF (0.55 g, 3 mmol) in toluene (30 mL) was stirred for 4 d at room temperature till Me$_3$SnF was almost consumed. After filtration, the filtrate was concentrated to ca. 10 mL in vacuum and kept at 4 ºC for a week to

afford colorless crystals. All spectroscopy confirmed the same compound as that obtained from method 1.

{[ArNH(CH$_2$)$_3$NAr]Al(μ-S)}$_2$ (3)

A suspension of **1** (1.48 g, 3 mmol) and elemental S (0.096 g, 3 mmol) in toluene (30 mL) was heated to 80 ºC and stirred for 12 h. After filtration, the orange-red filtrate was concentrated to ca. 10 mL and kept at 4 ºC for 48 h to afford light yellow crystals of **3**·toluene.

Yield: 1.00 g, 67%. M.p. 278−279 ºC (> 250 ºC, decompose).

^{1}H NMR (200.13 MHz, 300 K, C_6D_6, ppm): δ = 1.17, 1.22 (d, 48H, CH*Me*$_2$), 1.36 (s, 2H, N*H*), 1.78 (m, 4H, NCH$_2$C*H*$_2$), 2.1 (s, 3H, *Me*Ph), 3.00 (t, 8H, NC*H*$_2$), 3.38 (sept, 8H, C*H*Me$_2$), 6.96−7.04 (m, 5H, Me*Ph*), 7.02−7.10 (m, 12H, Ar−*H*).

MS (EI): *m*/*z* = 904 [*M*$^+$].

IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 3190 (NH).

$C_{61}H_{90}Al_2N_4S_2$ (996.8) (**3**·toluene): calcd. C 73.50, H 9.10, N 5.62; found: C 73.25, H 8.90, N 5.07.

{[ArNH(CH$_2$)$_3$NAr]Al(μ-Se)}$_2$ (4)

A suspension of **1** (1.44 g, 3 mmol) and elemental gray Se powder (0.24 g, 3 mmol) in toluene (30 mL) was refluxed for 12 h and almost all the selenium was consumed. In the course of hot filtration, the yellowish crystals were grown from the orange filtrate, which were collected by filtration. (0.10 g). The mother liquor was concentrated to ca. 10 mL and kept at 4 ºC for 24 h to afford another crop of yellowish crystals of **4**·2 toluene (1.00 g).

Total yield: 1.10 g (62%). M.p. 291 ºC (> 259 ºC, decompose).

^{1}H NMR (200.13 MHz, 300 K, C_6D_6, ppm): δ = 1.17, 1.22 (d, 48H, CH*Me*$_2$), 1.36 (s, 2H, N*H*), 1.78 (m, 4H, NCH$_2$C*H*$_2$), 2.1 (s, 6H, *Me*Ph), 3.00 (t, 8H, NC*H*$_2$), 3.38 (sept, 8H, C*H*Me$_2$), 6.94−7.04 (m, 10H, Me*Ph*), 7.02−7.10 (m, 12H, Ar−*H*).

^{77}Se NMR (500 MHz, 300 K, C_6D_6, $CDCl_3$, or C_7D_8, ppm): no resonances were observed.

MS (EI): *m*/*z* = 998 [*M*$^+$].

IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 3187 (NH).

$C_{68}H_{98}Al_2N_4Se_2$ (1182.9) (**4**·2toluene): calcd. C 69.04, H 8.35, N 4.74; found: C 68.79, H 8.22, N 4.63.

{[ArNH(CH$_2$)$_3$NAr]Al(μ-Te)}$_2$ (5)

A suspension of **1** (1.44 g, 3 mmol) and elemental Te powder (0.39 g, 3 mmol) in toluene (40 mL) was refluxed for 5 d and there still remained small amounts of unreacted Te powder. After filtration, the green-yellow filtrate was concentrated to ca. 10 mL and to it *n*-hexane (5 mL) was added. The solution was kept at 4 ºC for 24 h to afford green-yellow crystals of **5**·toluene.

Yield: 0.85 g, 48%. M.p. 320 ºC (decompose).

^{1}H NMR (200.13 MHz, 300 K, C_6D_6, ppm): δ= 1.17, 1.22 (d, 48H, CH*Me*$_2$), 1.35 (s, 2H, N*H*), 1.75 (m, 4H, NCH$_2$C*H*$_2$), 2.1 (s, 3H, *Me*Ph), 3.00 (t, 8H, NC*H*$_2$), 3.37 (sept, 8H, C*H*Me$_2$), 6.94–7.04 (m, 5H, Me*Ph*), 7.02–7.10 (m, 12H, Ar–*H*).

MS (EI): *m*/*z* = 1096 [M^+].

IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 3185 (NH).

$C_{61}H_{90}Al_2N_4Te_2$ (1188.1) (**5**·toluene): calcd. C 61.67, H 7.63, N 4.71; found: C 61.72, H 7.61, N 4.76.

LAlClMe (6)

To a toluene solution (80 mL) of LH (8.36 g, 20 mmol) at 0 ºC *n*-BuLi (2 M, 10 mL, 20 mmol) was added dropwise. The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was cooled to –78 ºC and $AlCl_2Me$ (1 M, 20 mL, 20 mmol) was added. The resulting suspension was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiCl was removed by filtration and the filtrate was dried *in vacuo* and washed with *n*-hexane to yield crystalline solid of **6**.

Yield: 9.1 g, 92%. M.p. 191–192 ºC.

^{1}H NMR (300.13 MHz, 298 K, C_6D_6, ppm): δ = –0.64 (s, 3 H, Al-*Me*), 1.00 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.19 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.28 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.46 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.54 (s, 2 x 3 H, β-*Me*), 3.21 (sept, 2 x 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.77 (sept, 2 x 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.98 (s, 1 H, γ-C*H*), 7.00–7.10 (m, 6 H, Ar–*H*).

MS (EI): *m*/*z* (%): 494.3 (3, [M^+]), 479.3 (100, [M^+ – Me]).

$C_{30}H_{44}AlClN_2$ (495.13): calcd. C 72.77, H 8.96, N 5.66; Found: C 72.32, H 8.74, N 5.71.

LAlClI (7)

A toluene solution (80 mL) of **6** (7.43 g, 15 mmol) and I_2 (3.81 g, 15 mmol) was stirred for 5 d. The solution was concentrated (ca 20 mL) and kept at 4 ºC for 24 h. The very light yellow crystals of **7** were formed and collected (5.5 g). The mother liquor was concentrated (ca 5 mL

) to afford a second crop of **7** (1.7 g).

Total yield: 7.2 g (79%). M.p. 200–203 ºC.

^{1}H NMR (300.13 MHz, 298 K, C_6D_6, ppm): δ = 1.02 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.12 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.41 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.42 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.52 (s, 2 x 3 H, *β-Me*), 3.28 (sept, 2 x 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.64 (sept, 2 x 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.96 (s, 1 H, γ-C*H*), 7.04–7.14 (m, 6 H, Ar–*H*).

MS (EI): *m/z* (%): 606 (1, [M^+]), 571 (4, [M^+ – Cl], 479 (100, [M^+ – I]).

$C_{29}H_{41}AlClIN_2$ (606.97): calcd. C 57.34, H 6.81, Cl 5.32, I 20.91, N 4.62; Found: C 58.00, H 6.86, Cl 5.14, I 19.23, N 4.70.

[LAlCl(*μ*-OH)]$_2$ (8)

To a mixture of **7** (0.61 g, 1 mmol) and [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (**:C**, 0.18 g, 1 mmol) in toluene (40 mL) at 0 ºC, distilled H_2O (18 μL, 1 mmol) was added. The suspension was allowed to warm to room temperature and stirred for 12 h. The insoluble solid was removed by filtration and the filtrate was dried *in vacuo* and extracted with *n*-hexane (10 mL). The extract was kept at 4 ºC to afford colorless crystals of **8**. X-ray quality crystals of **8** were grown from *n*-hexane and contained one molecule of *n*-hexane.

Yield: 0.35 g, 70%. M.p. > 177 ºC (decomp.).

^{1}H NMR (500.13 MHz, 298 K, C_6D_6, ppm): δ = 0.72 (s, 2 H, O*H*), 1.12 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.13 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.33 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.48 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.66 (s, 2 x 3 H, *β-Me*), 3.42 (sept, 2 x 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.47 (sept, 2 x 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.90 (s, 1 H, γ-C*H*), 7.04–7.12 (m, 6 H, Ar–*H*).

^{1}H NMR (200.13 MHz, 298 K, D_8-toluene, ppm): δ = 0.69 (s, 2 H, O*H*), 1.12 (d, 4 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.33 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.46 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.58 (s, 2 x 3 H, *β-Me*), 3.40 (sept, 4 x 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.94 (s, 1 H, γ-C*H*), 6.96–7.20 (m, 6 H, Ar–*H*).

^{27}Al NMR (78.20 MHz, 298 K, C_6D_6, ppm): no resonances were observed.

MS (EI): *m/z* (%): 496.3 (50, [M^+/2]), 478.3 (16, [M^+/2 – OH – 1], 461.3 (100, [M^+/2 – Cl]).

IR (KBr plate, Nujol mull, cm^{-1}): ν = 3459 (broad, OH).

$C_{58}H_{84}Al_2Cl_2N_4O_2$ (994.21): calcd. C 70.07, H 8.52, N 5.64; Found: C 69.34, H 8.69, N 5.34.

LAl(OH)$_2$ (9)

The synthetic procedure for **9** resembled that of **8** with the starting materials **8**, [CN(*i*Pr)C_2Me_2N(*i*Pr)], and H_2O in molar ratio of 1 : 2 : 2. After workup, by filtration to remove insoluble solids and drying *in vacuo* the *n*-hexane extract was kept at 4 ºC for 3 d to afford colorless crystals of **9** (25%). The spectrometric and spectroscopic data (EI-MS, IR, ^{1}H NMR) are almost the same as those described in literature. The characteristic data for the Al–OH functionality are listed here: ^{1}H NMR (300.13 MHz, 298 K, D_8-toluene, ppm): δ = 0.27 (s, 2 x 1 H, O*H*); IR (KBr plate, Nujol mull, cm^{-1}): ν = 3448 (broad, OH). The X-ray single crystal diffraction analysis confirms the same set of data reported for complex **9**.

[LAlO]$_2$ (10)

A toluene solution (20 mL) of LAl (0.44 g, 1 mmol) in 100 mL Schlenk flask was cooled to –78 ºC. The N_2 atmosphere in the flask was exchanged to O_2 (O_2 gas was predried with P_4O_{10}). In the course of stirring and warming to room temperature the color of the solution slowly changed from red to orange, to yellow, and finally to very light yellow, and at ca. –15 ºC a colorless crystalline solid started to form from the very light yellow solution. After additional stirring for 2 h, the solvent was removed *in vacuo* and the residue was washed with *n*-hexane (2 mL) to give crystalline **10**.

Yield: 0.37 g (80%). M.p. 314–315 ºC.

^{1}H NMR (C_6D_6, 298 K, 500.13 MHz, ppm): δ = 0.22 (d, $^3J_{HH}$ = 6.7 Hz, 2 × 3H, CH*Me*$_2$), 1.07 (d, $^3J_{HH}$ = 6.7 Hz, 2 × 3H, CH*Me*$_2$), 1.21 (d, $^3J_{HH}$ = 6.7 Hz, 2 × 3H, CH*Me*$_2$), 1.27 (d, $^3J_{HH}$ = 6.7 Hz, 2 × 3H, CH*Me*$_2$), 1.28 (d, $^3J_{HH}$ = 6.7 Hz, 2 × 3H, CH*Me*$_2$), 1.36 (s, 2 x 3H, β-C*H*$_3$), 1.39 (d, $^3J_{HH}$ = 6.7 Hz, 2 × 3H, CH*Me*$_2$), 1.45 (d, $^3J_{HH}$ = 6.7 Hz, 2 × 3H, CH*Me*$_2$), 1.49 (d, $^3J_{HH}$ = 6.7 Hz, 2 × 3H, CH*Me*$_2$), 1.52 (s, 2 x 3H, β-C*H*$_3$), 2.63 (sept, $^3J_{HH}$ = 6.7 Hz, 2 × 1H, C*H*Me$_2$), 3.22 (sept, $^3J_{HH}$ = 6.7 Hz, 2 × 1H, C*H*Me$_2$), 3.57 (sept, $^3J_{HH}$ = 6.7 Hz, 2 × 1H, C*H*Me$_2$), 3.83 (sept, $^3J_{HH}$ = 6.7 Hz, 2 × 1H, C*H*Me$_2$), 4.71 (s, 2 x 1H, γ-C*H*), 6.98–7.10, 7.15–7.31 (m, 12H, Ar–*H*).

^{13}C NMR (C_6D_6, 298 K, 125.8 MHz, ppm): δ = 22.2, 23.4, 24.2, 24.5, 25.0, 25.7, 26.4, 26.8, 27.2, 27.7, 29.1, 31.5, 32.4 (*C*H*Me*$_2$ and β-*C*H$_3$), 71.4 (*C*HMe$_2$), 97.8 (γ-*C*), 122.7, 124.2, 125.3, 125.7, 126.9, 127.7, 128.9, 142.0, 143.7, 145.7, 146.2, 148.1 (Ar–C_6H$_3$), 168.1 (*C*N).

MS (EI) (*m/z* (%)): 920.4 (30) [M^+], 403.3 (100) [L – Me].

$C_{58}H_{82}Al_2N_4O_2$ (921.29) (%): calcd. C 75.62, H 8.97, N 6.08; found C 75.20, H 9.02, N 6.21.

[LAl(OH)]$_2$(μ-O) (11):

To a suspension of **10** in toluene (30 mL) one equiv of H_2O was added at 0 ºC. The mixture

was allowed to warm to room temperature and stirred for 12 h to give a clear solution. All volatiles were removed and the residue was recrystallized in toluene/*n*-hexane at –26 ºC. The colorless crystals of **11**·1.5 *n*-hexane were obtained and determined by X-ray structural analysis. The cell parameters are almost the same as those for **11**·*n*-hexane·0.5 toluene. **11**·1.5 *n*-hexane: a = 13.677(1), b = 21.289(1), c = 23.014(1) Å, β = 104.69(1)º, V = 6482(1) Å^3; **11**·*n*-hexane·0.5 toluene: a = 13.731(3), b = 21.352(4), c = 22.877(5) Å, β = 103.58(3)º, V = 6520(1) Å^3.

{HC[(CMe)(NAr)][(CMe)(N-C$_6$H$_3$-2-*i*Pr-6-CH(CH$_2$)(Me)]}Al(NHAr'') (**12**),

[{HC[(CMe)(NAr)][(CMe)(N-C$_6$H$_3$-2-*i*Pr-6-CH(CH$_2$)(Me)]}Al(μ-OH)]$_2$ (**13**)

The reaction procedure is the same as that in the preparation of **25** and **26**, and LAl (0.47 g, 1.07 mmol) and N_3Ar'' (0.38 g, 1.07 mmol) are used. After workup, the solution was dried in vacuum and the residue was washed with *n*-hexane (2 mL) to afford colorless crystalline solids. The melting point is 218–219 ºC, however, the proton NMR spectrum indicates two sets of resonances, which may correspond two different compounds. By recrystallization in *n*-hexane/toluene, compounds **12** and **13** are isolated one by one both as colorless crystals.

12: yield: 0.48 g, 56%. M.p. 194–195 ºC.

^{1}H NMR (300.13 MHz, C_6D_6, 298 K, ppm): δ = –0.94 (dd, 1 H, $^2J_{HH}$ = −15.1 Hz, $^3J_{HH}$ = 7.7 Hz, Al–C*H*$_2$), –0.19 (dd, 1H, $^2J_{HH}$ = −15.1 Hz, $^3J_{HH}$ = 2.0 Hz, Al–C*H*$_2$), 0.66, 0.90, 0.97, 1.14, 1.18, 1.19, 1.22 (d, 7 x 3 H, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.44, 1.52 (s, 2 x 3 H, β-C*H*$_3$), 1.59, 1.76, 2.13, 2.19, 2.25, 2.34 (s, 6 x 3 H, Ar''–*Me*), 2.50, 2.79, 3.33 (sept, 3 x 1 H, $^3J_{HH}$ = 6.6 Hz, C*H*(CH$_3$)$_2$), 3.04 (m, 1 H, C*H*(CH$_3$)(CH$_2$)), 3.47 (s, 1 H, N*H*), 4.83 (s, 1 H, γ-C*H*), 6.62–7.20 (m, 13 H, Ar–*H*).

^{13}C NMR (125.76 MHz, C_6D_6, 298 K, ppm): δ = 20.25, 21.06, 21.13, 21.17, 22.16, 22.25, 23.00, 24.31, 24.77, 24.83, 24.84, 24.95, 25.13, 26.05, 26.90, 27.66, 28.08, 28.72, 31.91, 40.37 (β-*C*H$_3$, *C*H(*C*H$_3$)$_2$, *C*H(*C*H$_3$)(CH$_2$), Ar''–*Me*), 98.66 (γ-*C*H), 116.28, 118.60, 124.64, 124.72, 125.22, 127.43, 129.00, 129.40, 136.88, 137.04, 140.46, 141.46, 144.44, 144.80, 146.06, 146.27, 148.89 (Ar–*C*), 131.2 (br, Al–*C*), 169.97 (*C*N).

IR (KBr plate, Nujol mull, cm^{-1}): ν = 3265 (NH).

MS (EI): *m/z* (%): 771.7 (10, [M^+]), 443.4 (100, [M^+ − NHAr' − 1].

$C_{53}H_{66}AlN_3$ (771.743): calcd. C 82.45, H 8.62, N 5.44. Found: C 82.32, H 8.55, N 5.51.

13: yield: 0.23 g, 23%. M.p. 333–335 ºC.

^{1}H NMR (300.13 MHz, C_6D_6, 298 K, ppm): δ = –1.69 (t, 1 H, $^2J_{HH}$ = −14.2 Hz, $^3J_{HH}$ = 14.2 Hz, Al–C*H*$_2$), –0.35 (dd, 1 H, $^2J_{HH}$ = −14.2 Hz, $^3J_{HH}$ = 3.5 Hz, Al–C*H*$_2$), 0.29 (s, 2 x 1 H, O*H*), 0.74, 0.86, 0.90, 1.03, 1.17, 1.28, 1.32 (d, 7 x 3 H, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.42, 1.59 (s, 2 x 3 H, β-C*H*$_3$), 2.47, 2.78, 2.99 (sept, 3 x 1 H, $^3J_{HH}$ = 6.6 Hz, C*H*(CH$_3$)$_2$), 2.60 (m, 1 H, C*H*(CH$_3$)(CH$_2$)), 4.93 (s, 1 H, γ-C*H*), 6.80–7.20 (m, 12 H, Ar–*H*).

^{13}C NMR (125.76 MHz, C_6D_6, 298 K, ppm): δ = 20.59, 20.87, 21.26, 21.90, 22.44, 22.89, 24.06, 24.33, 24.97, 25.42, 26.60, 26.89, 28.37, 28.53, 31.91, 33.79 (β-*C*H$_3$, *C*H(*C*H$_3$)$_2$, *C*H(*C*H$_3$)(CH$_2$)), 100.09 (γ-*C*H), 116.55, 123.91, 124.68, 126.88, 127.81, 132.10, 141.46, 143.29, 144.11, 145.52, 146.16, 148.30 (Ar–*C*), 134.2 (br, Al–*C*), 168.11 (*C*N).

IR (KBr plate, Nujol mull, cm^{-1}): ν = 3400 (br., OH).

MS (EI): *m/z* (%): 920.6 (2, [M^+]), 887.6 (100, [M^+ − 2 Me – 2 H −1].

$C_{58}H_{80}AlN_4O_2$ (921.234): calcd. C 75.62, H 8.97, N 6.08. Found: C 75.48, H 8.85, N 6.11.

After the collection of crystals of **12** and **13**, the mother liquor was kept at 4 ºC for three weeks. A small amounts of colorless crystals of H_2NAr' were obtained and collected by filtration.

^{1}H NMR (500.13 MHz, C_6D_6, 298 K, ppm): δ = 1.35 (s, br, 2 H, N*H*$_2$), 2.06 (s, 4 x 3 H, *o*-Ar'–*Me*), 2.20 (s, 2 x 3 H, *p*-Ar'–*Me*), 6.84–6.87, 7.07–7.10 (m, 7 H, Ar–*H*).

^{13}C NMR (125.76 MHz, C_6D_6, 298 K, ppm): δ = 20.53 (*o*-Ar'–*Me*), 21.19 (*p*-Ar'–*Me*), 128.88, 129.03, 130.26, 135.33, 136.43, 137.17, 142.53, 147.95 (Ar–*C*).

IR (KBr plate, Nujol mull, cm^{-1}): ν = 3468, 3472 (NH).

Correct elemental analysis.

[HC{C(CH$_2$)NAr}(CMeNAr)]AlH[CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (14)

Method A: The suspension of LAlI$_2$ (2.08 g, 3.0 mmol) and finely divided potassium (0.25 g, 6.3 mmol) in toluene (50 mL) was stirred violently for 3 d at room temperature till all the potassium disappeared. After filtration the dark-red filtrate was slowly dried in vacuum and some red microcrystals of LAl were observed depositing on the wall of the flask. To the remaining solid [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (0.36 g, 2 mmol) was added. The mixture was allowed slowly to heat to ca. 120 °C and kept for 5 h. After cooling to room temperature, the yellow product was extracted with hot toluene (30 mL) and the extract was kept at room temperature for 24 h to afford X-ray quality colorless block crystals of **14**, which were collected by filtration (0.42 g). The mother liquor was concentrated (ca. 5 mL) and kept at 4 °C for 24 h to give another crop of colorless crystals (0.25 g).

Total yield of **14**: 0.67 g (47%, based on [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)]). M.p. 298–300 °C (> 250 °C

decomp.).

^{1}H NMR (300.13 Hz, 300 K, C_6D_6, ppm): δ = 0.38, 0.50, 0.76, 0.82, 1.19, 1.32, 1.46, 1.50, 1.53, 1.55, 1.57, 1.59 (d, 12 × 3H, CH*Me*$_2$ and N(CH*Me*$_2$)), 1.38, 1.62 (s, 2 × 3H, C_2*Me*$_2$), 1.72 (s, 3H, β-C*H*$_3$), 3.30, 3.98 (s, 2 × 1H, β-C*H*$_2$), 3.28, 3.62, 4.18, 4.26 (sept, 4 × 1H, C*H*Me$_2$), 4.80 (br, 1H, Al–*H*), 5.60 (s, 1H, γ-C*H*), 5.44, 5.62 (sept, 2 × 1H, N(C*H*Me$_2$)), 7.10–7.38 (m, 6H, Ar–*H*).

^{13}C NMR (300.13 Hz, 300 K, C_6D_6, ppm): δ = 9.9, 10.0 (C_2*Me*$_2$), 20.7, 21.1, 21.4, 22.0, 23.3, 23.7, 23.8, 24.4, 24.5, 24.7, 25.6, 25.7, 26.4, 27.1, 27.7, 28.4, 28.9 (N(CH*Me*$_2$), *C*HMe$_2$, CH*Me*$_2$ and β-*C*H$_3$), 50.9, 53.0 (N(*C*HMe$_2$)), 80.8 (β-*C*H$_2$), 106.6 (γ-*C*), 123.0, 124.5, 124.7, 124.9, 125.6, 126.6, 127.8, 128.5, 129.3, 143.4, 144.7, 145.6, 146.1, 147.2, 148.4, 149.0 (Ar–*C*, *C*N and *C*$_2$Me$_2$), 154.5 (Al–*C*).

^{27}Al NMR (79.2 Hz, 300 K, toluene-d_8, ppm): no resonances were observed.

IR (KBr plate, Nujol, cm^{-1}): ν = 1809 (m, Al–H), ν = 1619 (m, C=C).

MS (EI) (*m/z* (%)): 624 (5) [*M*$^+$], 609 (40) [*M*$^+$ − Me], 581 (100) [*M*$^+$ − *i*Pr].

$C_{40}H_{61}AlN_4$ (624.94): calcd. C 76.87, H 9.84, N 8.97; found C 77.07, H 9.55, N 8.86.

Method B: The suspension of $LAlI_2$ (2.08 g, 3.0 mmol), [CN(*i*Pr)C_2Me$_2$N(*i*Pr)] (0.54 g, 3 mmol) and finely divided potassium (0.25 g, 6.3 mmol) in toluene (50 mL) was stirred intensively for 3 d at room temperature till all the potassium disappeared. After filtration the orange filtrate was concentrated (ca. 20 mL) and *n*-hexane (20 mL) was added. The solution was kept at 4 °C for one week to afford colorless block crystals (0.72 g). The mother liquor was further concentrated (ca. 5 mL) and kept at 4 °C for 2 d to give another crop of colorless crystals (0.32 g). Total yield of **14**·toluene: 1.04 g (48%). The IR, ^{1}H and ^{13}C NMR spectral data are essentially the same as those of **14** except for one extra molecule of toluene.

[HC{C(CH$_2$)NAr}(CMeNAr)]AlH[CN(Me)C$_2$Me$_2$N(Me)] (15)

Compound **15** was prepared in a similar manner (method A) as **14**. $LAlI_2$ (2.08 g, 3.0 mmol), finely divided potassium (0.25 g, 6.3 mmol) and [CN(Me)C_2Me$_2$N(Me)] (0.24 g, 2.0 mmol) were used. The extract (10 mL) was added to *n*-hexane (10 mL) and kept at –26 °C for 48 h to afford colorless crystals of **15**.

Yield: 0.42 g, 25%, based on [CN(Me)C_2Me$_2$N(Me)]. M.p. 252–253 °C.

^{1}H NMR (300.13 Hz, 300 K, toluene-d_8, ppm): δ = 1.45, 1.47 (s, 2 × 3H, C_2*Me*$_2$), 0.29, 0.30, 1.16, 1.46, 1.58, 1.60, 1.61, 1.62 (d, 8 × 3H, CH*Me*$_2$), 1.69 (s, 3H, β-C*H*$_3$), 3.70, 3.75 (s, 2 ×

3H, N(*Me*)), 3.10, 3.85 (s, 2 × 1H, β-CH_2), 3.21, 3.25, 4.15, 4.21 (sept, 4 × 1H, C*H*Me$_2$), 4.80 (br, 1H, Al–*H*), 5.39 (s, 1H, γ-C*H*), 7.04–7.38 (m, 6H, Ar–*H*).

^{13}C NMR (300.13 Hz, 300 K, toluene-d$_8$, ppm): δ = 7.9, 8.0 (C$_2$*Me*$_2$), 23.6, 24.0, 24.2, 24.3, 24.8, 24.9, 25.4, 25.8, 26.0, 26.4, 26.5, 27.1, 27.8, 28.7, 29.0 (N(*Me*), *C*HMe$_2$, CH*Me*$_2$ and β-*C*H$_3$), 80.1 (β-*C*H$_2$), 102.3 (γ-*C*), 122.9, 123.7, 124.2, 124.6, 124.9, 125.1, 125.3, 127.7, 128.0, 143.2, 143.8, 145.4, 146.3, 147.4, 148.2, 149.0 (Ar–*C*, *C*N and *C*$_2$Me$_2$), 155.2 (Al–*C*).

MS (EI) (*m/z* (%)): 568 (15) [M^+], 553 (100) [M^+ – Me].

IR (KBr plate, Nujol, cm^{-1}): ν = 1810 (m, Al–H), ν = 1616 (m, C=C).

$C_{36}H_{53}AlN_4$ (568.83): calcd. C 76.01, H 9.29, N 9.85; found C 76.50, H 9.60, N 9.40.

LAl(N=CPh$_2$)$_2$ (16)

A solution of N_2CPh_2 (0.37 g, 1.90 mmol) in toluene (15 mL) was added to a solution of LAl (0.42 g, 0.94 mmol) in toluene (25 mL) at room temperature. The mixture was slowly heated to 60 °C and kept for 12 h, and a yellow colored solution developed. All volatiles were removed in vacuum. The residue was washed with *n*-hexane (5 mL) to afford an orange-yellow crystalline solid of **16**. X-ray quality crystals were obtained by recrystallization from a 1:1 *n*-hexane/ether solution at 4 °C for one week.

Yield: 0.36 g, 48%. M.p. 344–346 °C.

^{1}H NMR (300.13 Hz, 300 K, C_6D_6, ppm): δ = 0.82, 1.02 (d, 8 × 3 H, CH*Me*$_2$), 1.64 (s, 2 × 3 H, β-C*H*$_3$), 3.21 (sept, 4 × 1H, C*H*Me$_2$), 5.28 (s, 1 H, γ-C*H*), 6.92–7.00 (m, 2 × 5 H, *Ph*), 7.00–7.08 (m, 2 × 5 H, *Ph*), 7.18–7.32 (m, 6H, Ar–*H*).

^{13}C NMR (300.13 Hz, 300 K, C_6D_6, ppm): δ = 23.8, 24.4, 24.9, 28.5 (*C*HMe$_2$, CH*Me*$_2$, β-*C*H$_3$), 98.8 (γ-*C*), 124.5, 126.9, 127.6, 127.6, 127.9, 128.1, 128.3, 128.3, 129.4, 142.4, 143.1, 144.7 (Ar–*C*, *Ph*), 166.9 (N*C*Ph$_2$), 171.0 (*C*N).

MS (EI) (*m/z* (%)): 805 (20) [M^+], 790 (30) [M^+ – Me], 624 (100) [M^+ – NCPh$_2$].

IR (KBr plate, Nujol, cm^{-1}): ν = 1667 (w, C=C), ν = 1624, 1554 (w, C=N).

$C_{55}H_{61}AlN_4$ (805.10): calcd. C 82.05, H 7.64, N 6.96; found C 82.11, H 7.74, N 7.05.

LAl[N(H)-*o*-C$_6$H$_4$N(Ph)] (17)

Method A. A toluene solution (30 mL) of LAl (0.22 g, 0.5 mmol) and PhNNPh (0.09 g, 0.5 mmol) was stirred and allowed to heat slowly to 80 ºC for 5 h. The color of the solution changed from red to orange. The solution was reduced in vacuum (ca 10 mL) and *n*-hexane was added (10 mL). Keeping this solution at 4 ºC for one week the orange X-ray quality

crystals of **17** were obtained (0.15 g) and collected. The mother liquor was concentrated again (ca. 4 mL) and *n*-hexane added (8 mL). Another crop of orange crystals (0.10 g) was obtained by keeping the solution at –26 °C for 24 h.

Total yield: 0.25 g, 81%. M.p. 260–261 ºC.

^{1}H NMR (300.13 MHz, 298 K, C_6D_6, ppm): δ = 0.90 (d, $^3J_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH_3)$_2$), 0.92 (d, $^3J_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH_3)$_2$), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH_3)$_2$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH_3)$_2$), 1.47 (s, 2 x 3 H, β-CH_3), 3.05 (sept, $^3J_{HH}$ = 6.8 Hz, 2 x 1 H, CH(CH$_3$)$_2$), 3.06 (s, 1 H, NH), 3.14 (sept, $^3J_{HH}$ = 6.8 Hz, 2 x 1 H, CH(CH$_3$)$_2$), 5.12 (s, 1 H, γ-CH), 6.31–6.34 (m, 1 H), 6.58–6.66 (m, 2 H), 6.82–6.92 (m, 3 H), 6.94–7.02 (m, 4 H), 7.22–7.30 (m, 4 H), 7.48–7.52 (m, 1 H) (Ar–H and Ph–H).

^{13}C {^{1}H} NMR (125.77 HMz, 298 K, C_6D_6, ppm): δ = 23.4, 24.2, 24.5, 24.9, 25.1, 28.3, 29.2 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 99.2 (γ-*C*), 112.3, 114.0, 115.1, 118.8, 124.0, 125.1, 127.9, 128.2, 129.0, 139.5, 143. 1, 143.7, 145.3, 148.8 (Ar–*C*, Ph–*C*), 171.5 (*C*N).

IR (KBr plate, Nujol mull, cm^{-1}): ν 3220 (NH).

MS (EI): m/z (%) 626 ([M^+],100).

$C_{41}H_{51}AlN_4$ (626.87): calcd. C 78.56, H 8.20, N 8.14; Found: C 78.23, H 8.18, N 8.24.

Method B. To a toluene solution (20 mL) of LAl[η^2-C_2(SiMe$_3$)$_2$] (0.62 g, 1 mmol) at –50 ºC was added a toluene solution (5 mL) of PhNNPh (0.18 g, 1 mmol). The mixture was allowed to warm to room temperature under stirring. The solution changed from black to orange. After continuing the stirring for 12 h the solution was dried in vacuum and washed with *n*-hexane (10 mL) to afford an orange crystalline solid, which was characterized as **17** by m.p. and EI-mass measurements.

LAl(η^2-C_2H_2) (18)

A toluene solution (30 mL) of LAl (0.22 g, 0.5 mmol) at reduced pressure was cooled to –78 ºC and exposed to dried C_2H_2. This mixture was kept in the temperature range of –78 ºC to –50 ºC for 2 h. An instant color change of the solution from red to orange was observed. All volatiles were removed and an orange crystalline solid of **18** was afforded. The X-ray single crystals of **18** were obtained by keeping the *n*-hexane/toluene solution of **18** at –26 ºC for one week.

Yield: > 95%. M.p. 219 ºC.

^{1}H NMR (500.13 MHz, 298 K, C_6D_6, ppm): δ = 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 4 x 3 H, CH(CH_3)$_2$), 1.46 (d, $^3J_{HH}$ = 6.9 Hz, 4 x 3 H, CH(CH_3)$_2$), 1.53 (s, 2 x 3 H, β-CH_3), 3.33 (sept, $^3J_{HH}$ = 6.9

Hz, 4 x 1 H, C*H*(CH_3)$_2$), 4.89 (s, 1 H, γ-C*H*), 7.02–7.12 (m, 6 H, Ar–*H*), 8.82 (s, 2 x 1 H, Al–η^2-CH_2).

^{13}C NMR (125.77 HMz, 298 K, C_6D_6, ppm): δ = 23.4, 24.4, 24.6, 28.9 (*C*H(*C*H_3)$_2$, β-*C*H_3), 96.5 (γ-*C*), 124.4, 138.8, 143.9 (Ar–*C*), 172.8 (*C*N), 177.2 (broad, Al–η^2-C_2).

^{27}Al NMR (77.13 MHz, 298 K, C_6D_6, ppm): the signal is too broad to be observed.

IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ 442.7(w), 529.1(w), 589.8(m), 613.5(w), 647.4(w), 712.7(m), 748.3(w), 758.5(w), 778.2(w), 801.0(s), 867.7(w), 893.9(w), 936.7(w), 1026.0(m), 1055.6(w), 1100.6(m), 1177.4(w), 1260.7(m), 1304.9(w), 1318.7(w), 1410.5(s), 1485.6(s), 1532.8(m), 1653.7(w).

MS (EI): *m/z* (%) 429.3 (100, [M^+ – Me – C_2H_2]), 455.3 (30, [M^+ – Me]), 469.3 (20, [M^+ – 1]).

$C_{31}H_{43}AlN_2$ (470.68): calcd. C 79.10, H 9.21, N 5.95; Found: C 79.43, H 9.18, N 6.03.

LAl(C≡CH)(CH=CH$_2$) (19)

The initial procedure (LAl (0.22 g, 0.5 mmol), C_2H_2 (excess), and toluene (30 mL)) is the same as the synthesis of **19**. At –50 ºC, the mixture was stirred and warmed to ambient temperature within 48 h, the color of the solution slowly turned to almost colorless. Then all volatiles were removed in vacuum and the residue was washed with *n*-hexane (2 mL) to afford colorless crystalline solid of **19**. The X-ray single crystals of **19** were grown from the *n*-hexane solution of **19** at 4 ºC within one week.

Yield: 0.22 g, 90%. M.p. 163–164 ºC.

^{1}H NMR (500.13 MHz, 298 K, D_8-toluene, ppm): δ = 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 2 x 3 H, CH(C*H*$_3$)$_2$), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 2 x 3 H, CH(C*H*$_3$)$_2$), 1.28 (d$^3J_{HH}$ = 6.8 Hz,, 2 x 3 H, CH(C*H*$_3$)$_2$), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 2 x 3 H, CH(C*H*$_3$)$_2$), 1.55 (s, 2 x 3 H, β-C*H*$_3$), 1.73 (s, 1 H, C≡C*H*), 3.23 (sept, $^3J_{HH}$ = 6.8 Hz, 2 x 1 H, C*H*(CH_3)$_2$), 3.81 (sept, $^3J_{HH}$ = 6.8 Hz, 2 x 1 H, C*H*(CH_3)$_2$), 4.91 (s, 1 H, γ-C*H*), 5.79 (dd, $^3J_{HH(trans)}$ = 20.9 Hz, $^2J_{HH}$ = 6.4 Hz, 1 H), 6.04 (dd, $^3J_{HH(cis)}$ = 16.5 Hz, $^2J_{HH}$ = 6.4 Hz, 1 H), 6.12 (dd, $^3J_{HH(trans)}$ = 20.9 Hz, $^3J_{HH(cis)}$ = 16.5 Hz, 1 H), (C*H*=CH_2), 6.97–7.12 (m, 6 H, Ar–*H*).

^{13}C NMR (125.76 HMz, 298 K, D_8-toluene, ppm): δ = 23.4, 24.5, 24.7, 24.8, 27.2, 28.2, 28.6 (*C*H(*C*H_3)$_2$, β-*C*H_3), 94.6 (broad, ≡*C*H), 98.4 (γ-*C*), 124.1, 124.8, 127.5, 128.8, 129.2, 137.1, 140.3, 143.7, 145.4 (Ar-*C*), 125.4, (=*C*H_2), 137.3 (broad, Al–*C*≡), 138.0 (broad, Al–*C*=), 170.6 (*C*N).

IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ 1992 (C≡C), 3277 (≡CH).

MS (EI): m/z (%) 469.4 (100, [M^+ – CH=CH_2]), 496.4 (15, [M^+]).

$C_{33}H_{45}AlN_2$ (496.72): calcd. C 79.80, H 9.13, N 5.64; Found: C 79.26, H 9.18, N 5.56.

LAl(C≡CPh)(CPh=CHPh) (20)

To a toluene solution (30 mL) of LAl(η^2-C_2Ph_2) (1.24 g, 2 mmol) was added a toluene solution (10 mL) of a little excess of HC≡CPh (0.33 mL, 3 mmol). The mixture was stirred for 12 h at room temperature and dried in vacuum, and then extracted with *n*-hexane (10 mL). The extract was kept at 4˚C for a week to afford colorless crystals of **20**·0.5 *n*-hexane.

Yield: 1.12 g, 73%. M.p. 187−190 ˚C.

^{1}H NMR (300.13 MHz, 298 K, C_6D_6, ppm): δ = 0.86~0.90 (m, 7 H, *n*-hexane), 1.11 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.24 (d, 4 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.35 (d, 2 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.61 (s, 2 x 3 H, β-CH_3), 3.44 (sept, 2 x 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.01 (sept, 2 x 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 5.08 (s, 1 H, γ-C*H*), 6.72 (broad, 1 H, C=C*H*), 6.40−6.52, 6.80−7.00 (m, 10 H, C(*Ph*)=CH(*Ph*)), 7.08−7.24, 7.42−7.54 (m, 6 H, Ar−*H*).

^{13}C NMR (125.76 HMz, 298 K, C_6D_6, ppm): δ = 14.3 (*n*-hexane), 23.0, 24.5, 24.8, 24.9, 26.1, 28.7, 29.2, 31.9 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 99.5 (γ-*C*), 106.6 (broad, ≡*C*Ph), 124.1, 124.2, 125.4, 126.4, 127.1, 127.4, 128.0, 129.6, 131.4, 132.0, 139.1, 141.3, 143.2, 145.9, 146.7 (Ph−*C*, Ar−*C*, =*C*), 144.4, 153.8 (broad, Al−*C*≡, Al−*C*=), 171.1 (*C*N).

IR (KBr plate, Nujol mull, cm^{-1}): ν 2124 (C≡C).

MS (EI): m/z (%) 545 (100, [M^+ − C(Ph)=CH(Ph)]), 724 (2, [M^+ − 1]).

$C_{54}H_{64}N_2Al$ (**20**·0.5*n*-hexane, 768.102): calcd. C 84.44, H 8.40, N 3.65; Found: C 84.81, H 8.42, N 3.61.

LAl[η-C(H)=C(H)-η-](NN=NAr') (21)

To a mixture of **18** (0.25 g, 0.5 mmol) and N_3Ar* (0.18 g, 0.5 mmol) at –50 ºC toluene (25 mL) was added. The suspension was stirred and allowed to warm to room temperature. After stirring for 12 h, the removal of solvent and washing with *n*-hexane (2 mL) afforded **21** as orange crystalline solid. The X-ray quality single crystals of **21**·0.5*n*-hexane were grown from the *n*-hexane/toluene solution of **21** at 4 ºC within 5 d.

Yield: 0.37 g, 90%. M.p. 215–216 ºC.

^{1}H NMR (300.13 MHz, 298 K, C_6D_8, ppm): δ = 1.02 (d, $^3J_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH_3)$_2$), 1.05 (d, $^3J_{HH}$ = 6.8 Hz, 2 x 3 H, CH(CH_3)$_2$), 1.16 (d$^3J_{HH}$ = 6.8 Hz,, 4 x 3 H, CH(CH_3)$_2$), 1.50 (s, 2 x 3 H, β-CH_3), 2.23 (s, 2 x 3 H), 2.27 (s, 4 x 3 H) (*Me*(in Ar')), 2.83 (sept, $^3J_{HH}$ = 6.8 Hz, 2 x 1 H, C*H*(CH$_3$)$_2$), 3.03 (sept, $^3J_{HH}$ = 6.8 Hz, 2 x 1 H, C*H*(CH$_3$)$_2$), 4.92 (s, 1 H, γ-C*H*), 5.03

(d, $^3J_{HH(cis)}$ = 7.6 Hz, 1 H), 7.51 (d, $^3J_{HH(cis)}$ = 7.6 Hz, 1 H) (*H*C=C*H*), 6.83, 6.97–7.12 (m), 7.15 (14 H, Ar–*H*, Ar*–*H,* Ar'–*H*).

^{13}C NMR (75.47 HMz, 298 K, C_6D_6, ppm): δ = 21.3, 22.3, 23.0, 23.2, 24.4, 24.7, 25.0, 25.8, 26.7, 29.1, 31.9 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$, *Me*(Ar')), 100.5 (γ-*C*), 114.8 (broad, Al–*C*=), 123.5, 123.8, 125.1, 130.9, 134.2, 136.0, 138.5, 141.6, 146.2, 147.3 (Ar–*C*, Ar*–*C,* Ar'–*C*), 162.4 (N–*C*(H)=), 171.9 (*C*N).

MS (EI): m/z (%) 417 (100, [M^+ – N_3Ar* – C_2H_2 – Al]), 825 (5, [M^+ – 1]).

$C_{55}H_{68}AlN_5$ (826.17): calcd. C 79.96, H 8.30, N 8.48; Found: C 79.28, H 8.38, N 8.42.

LAl[OC(O)C$_2$(Ph)$_2$] (22)

A toluene solution (30 mL) of LAl[η^2-C$_2$(Ph)$_2$] (0.62 g, 1 mmol) was exposed to predried CO_2 and stirred for 12 h. After workup, all volatiles were removed in vacuum and the residue was washed with *n*-hexane (10 mL) to give a colorless solid of **22**.

Yield: 0.47 g, 70%. M.p. 341–343 ºC (decomp.).

^{1}H NMR (300.13 MHz, 298 K, C_6D_6, ppm): δ = 0.82 (d, $^3J_{HH}$ = 6.7 Hz, 2 x 3 H, CH(C*H*$_3$)$_2$), 0.93 (d, $^3J_{HH}$ = 6.7 Hz, 2 x 3 H, CH(C*H*$_3$)$_2$), 1.10 (d, $^3J_{HH}$ = 6.7 Hz, 2 x 3 H, CH(C*H*$_3$)$_2$), 1.52 (d, $^3J_{HH}$ = 6.7 Hz, 2 x 3 H, CH(C*H*$_3$)$_2$), 1.53 (s, 2 x 3 H, β-C*H*$_3$), 2.90 (sept, $^3J_{HH}$ = 6.7 Hz, 2 x 1 H, C*H*(CH$_3$)$_2$), 3.60 (sept, $^3J_{HH}$ = 6.7 Hz, 2 x 1 H, C*H*(CH$_3$)$_2$), 5.00 (s, 1 H, γ-C*H*), 6.26–6.28 (m), 6.78–7.20 (m) (16 H, Ar–*H* and Ph–*H*).

^{13}C {^{1}H} NMR (125.77 HMz, 298 K, C_6D_6, ppm): δ = 20.7, 23.3, 23.6, 28.6 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 94.2 (γ-*C*), 123.6, 125.8, 127.7, 128.2, 129.3, 141.2, 142.8, 143.0, 145.8 (Ar–*C*, Ph–*C,* AlC(Ph)=*C*(Ph)), 143.4 (Al–*C*), 161.5 (*C*=O), 172.8 (*C*N).

MS (EI): m/z (%) 666.3 ([M^+], 15), 651.3 ([M^+ – Me], 100).

$C_{44}H_{51}AlN_2O_2$ (666.89): calcd. C 79.25, H 7.71, N 4.20; Found: C 78.92, H 7.54, N 4.26.

LAl[OC(O)C$_2$(SiMe$_3$)$_2$] (23)

Compound **23** was prepared in a similar manner as that of **22**. The spectral data are recoreded in reference 155. The X-ray quality crystals of **23** were obtained by crystallizing the crude product from a mixture of solvents (toluene : ether : *n*-hexane = 0.2 : 1 : 1).

LAl(μ-S)(η-SC(SiMe$_3$)=C=C(SiMe$_3$)-η-)AlL (24)

Neat carbon disulfide (0.038 g, 0.5 mmol) was added to a solution of LAl[η^2-C$_2$(SiMe$_3$)$_2$] (0.62 g, 1 mmol) in toluene (20 mL) at –78 ºC. In the course of warming to room temperature, the color of the reaction mixture changed from red-black to green, to yellow green, and finally

to yellow. After additional stirring for 12 h, all volatiles were removed under vacuum and the residue was washed with *n*-hexane (20 mL) to give a yellow solid. The yellow solid was dissolved in a hot mixture of solvents (2 toluene : 1 ether) (15 mL) and then kept at r.t. for 72 h to afford X-ray suitable single crystals of **24**·0.55toluene·0.45ether.

Yield: 0.35 g, 57%. M.p. 281−283 ˚C.

^{1}H {^{13}C} NMR ([D$_8$]toluene, 500.13 MHz, 300 K, ppm): δ = 0.39, 0.47 (s, 2 × 9 H, Si*Me*$_3$), 0.88, 0.70, 0.83, 0.68, 1.19, 0.58, 1.39, 1.15, 1.31, 1.08 (d, $^{3}J_{HH}$ = 6.7 Hz, 10 × 3 H, CH*Me*$_2$), 1.15 (t, $^{3}J_{HH}$ = 6.9 Hz, 2.70 H, (C*H*$_3$CH$_2$)$_2$O), 1.25, 0.54, 1.33, 1.05 (d, $^{3}J_{HH}$ = 6.8 Hz, 4 × 3 H, CH*Me*$_2$), 1.14, 1.68 (d, $^{3}J_{HH}$ = 6.5 Hz, 2 × 3 H, CH*Me*$_2$), 1.48, 1.41, 1.40, 1.37 (s, 4 × 3 H, *β*-C*H*$_3$), 2.10 (s, 1.65 H, *Me*Ph), 3.17, 3.17, 3.10, 2.96, 2.93 (sept, $^{3}J_{HH}$ = 6.7 Hz, 5 × 1 H, C*H*Me$_2$), 3.13 (sept, $^{3}J_{HH}$ = 6.5 Hz, 1 H, C*H*Me$_2$), 3.26 (quartet, $^{3}J_{HH}$ = 6.9 Hz, 1.80 H, (CH$_3$C*H*$_2$)$_2$O), 3.29, 2.98 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2 × 1 H, C*H*Me$_2$), 4.95, 4.96 (s, 2 × 1 H, *γ*-C*H*), 6.82−7.21 (m, 12 H, Ar−*H*).

^{13}C NMR (CDCl$_3$, 500.13 MHz, 300 K, ppm): δ = 212.70 (C=*C*=C), 171.16, 170.66, 170.32, 168.54 (*C*N), 145.30, 145.16, 144.69, 144.29, 144.09, 143.72, 142.91, 142.50, 142.49, 142.42 141.46, 141.03, 126.58, 126.44, 126.10, 125.98, 124.84, 124.50, 124.42, 124.34, 124.27, 124.00, 123.95, 123.02 (Ar-*C*), 137.88, 129.04, 128.23, 125.30 (Me*Ph*), 100.18, 99.74 (*γ*-*C*), 80.60 (broad, Al-*C*=C=CS), 65.84 ((CH$_3$*C*H$_2$)$_2$O), 59.94 (C=C=*C*S), 30.04, 29.19, 28.73, 28.26, 28.20, 27.98, 27.81, 27.74, 27.57, 27.17, 25.93, 25.86, 25.69, 25.52, 25.35, 25.19, 25.05, 24.95, 24.94, 24.82, 24.81, 24.71, 24.54, 24.51, 24.39, 24.36, 23.71, 23.22 (*C*HMe$_2$, CH*Me*$_2$ and *β*-*C*H$_3$), 21.45 (*Me*Ph), 15.27 ((*C*H$_3$CH$_2$)$_2$O), 2.19, 0.89 (Si*Me*$_3$).

^{29}Si NMR (C$_6$D$_6$, 500.13 MHz, 300 K, ppm): δ = −5.51, −4.62 (*Si*Me$_3$).

IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1822 (C=C=C).

MS (EI): *m/z* (%): 1135 (60, [*M*$^+$]); 460 (100, [*M*$^+$ − {HC(CMeNAr)$_2$}Al − SC(SiMe$_3$)=C=C(SiMe$_3$) − Me − H].

C$_{72.65}$H$_{108.90}$Al$_2$N$_4$O$_{0.45}$S$_2$Si$_2$ (**24**·0.55toluene·0.45ether, 1219.82): calcd. C 71.53, H 9.00, N 4.59; Found: C 71.29, H 9.09, N 4.69.

LAl[N-C$_6$H$_3$-2-(2,6-*i*Pr$_2$C$_6$H$_3$)-6-(2,6-*i*Pr$_2$C$_6$H$_3$)] (25) and

{HC[(CMe)(NAr)][(CMe)(N-C$_6$H$_3$-2-*i*Pr-6-CH(CH$_2$)(Me)]}Al(NHAr) (26)

Pre-cooled toluene (25 mL) was added to a mixture of LAl (0.25 g, 0.56 mmol) and N$_3$Ar' (0.25 g, 0.56 mmol) at –78 ºC. The mixture was allowed to warm to room temperature and

stirred for 12 h. The light yellow solution was concentrated (5 mL), and to it *n*-hexane (10 mL) was added. The solution was kept at 4 ºC for three weeks to afford colorless crystals of **26**.

Yield: 0.12 g (24%). M.p. 381−383 ºC (> 320 ºC, decomp.).

^{1}H NMR (500.13 MHz, C_6D_6, 298 K, ppm): δ = −1.75 (t, 1H, $^2J_{HH}$ = −13.8 Hz, $^3J_{HH}$ = 13.8 Hz, Al−CH_2), −0.28 (dd, 1H, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 3.0 Hz, Al−CH_2), 0.36, 0.39, 0.50, 0.80, 1.15, 1.22, 1.30 (d, 7 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 0.93, 0.94, 1.08, 1.11 (d, 4 x 3 H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 1.25, 1.34 (d, 2 x 3 H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.31, 1.53 (d, 2 x 3 H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.45, 1.50 (s, 2 x 3 H, β-CH_3), 2.30 (sept, 1 H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$), 2.41, 2.80, 3.47 (sept, 3 x 1 H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 2.99, 3.39 (sept, 2 x 1 H, $^3J_{HH}$ = 6.7 Hz, CH(CH$_3$)$_2$), 3.07 (sept, 1 H, $^3J_{HH}$ = 6.6 Hz, CH(CH$_3$)$_2$), 2.56 (m, 1 H, CH(CH$_3$)(CH$_2$)), 3.41 (s, 1 H, NH), 4.82 (s, 1 H, γ-CH), 6.65 (m, 1 H, Ph−H), 6.92−7.00 (m, 3 x 1 H, Ph−H), 7.04−7.20 (m, 6 x 1 H, Ph−H), 7.20−7.32 (m, 4 x 1 H, Ph−H), 7.34−7.38 (m, 1 H, Ph−H).

^{13}C NMR (125.76 MHz, C_6D_6, 298 K, ppm): δ = 18.50 (br, Al−C), 21.64, 21.68, 22.10, 22.84, 22.98, 23.61, 23.83, 23.93, 24.41, 25.31, 25.45, 25.55, 26.31, 26.92, 26.98, 27.06, 27.25, 27.66, 28.53, 28.57, 29.97, 30.03, 31.23, 31.69, 34.04 (β-CH$_3$, CH(CH$_3$)$_2$, CH(CH$_3$)(CH$_2$)), 98.99 (γ-CH), 114.62, 122.23, 122.98, 123.08, 123.64, 124.65, 124.67, 125.06, 125.65, 125.93, 126.55, 126.88, 127.81, 127.92, 128.42, 131.23, 133.84, 138.21, 140.30, 141.50, 142.48, 143.51, 143.82, 145.58, 146.53, 147.62, 148.48, 148.53, 150.68, 150.94 (Ph−C), 169.40, 169.52 (CN).

IR (KBr plate, Nujol mull, cm^{-1}): ν = 3298 (NH).

MS (EI): *m/z* (%): 855 (10, [M^+ − 1]); 443 (100, [M^+ − NHAr'].

$C_{59}H_{78}AlN_3$ (855.42): calcd. C 82.76, H 9.18, N 4.91. Found: C 82.60, H 9.28, N 4.98.

After the collection of crystals of **26**, the mother liquor was kept at 4 ºC for additional three weeks. A crop of yellowish crystals of **25** were obtained and collected by filtration. Compound **25** has a similar decomposition temperature and melting point as those of **26**. Its EI mass spectroscopic data is also similar to that of **26**.

Yield: 0.21 g (42%).

^{1}H NMR (500.13 MHz, C_6D_6, 298 K, ppm): δ = 0.26, 0.53, 0.54, 1.46 (d, 4 x 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 0.81, 0.93, 1.01, 1.06, 1.11, 1.30 (d, 6 x 3 H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 0.86, 0.88, 1.14, 1.27, 1.39, 1.42 (d, 6 x 3 H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.30, 1.40 (s, 2 x 3 H, β-CH$_3$), 2.34, 3.33 (sept, 2 x 1 H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 2.64, 3.02, 3.18 (sept, 3 x 1 H, $^3J_{HH}$ = 6.7 Hz, CH(CH$_3$)$_2$), 3.12, 3.33, 3.33 (sept, 3 x 1 H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$), 2.43 (d, 1 H,

$^3J_{HH}$ = 6.4 Hz, Al–C*H*), 4.88 (s, 1 H, γ-C*H*), 5.41 (d, 1 H, $^3J_{HH}$ = 9.4 Hz, AlCH–C*H*), 6.08 (dd, 1 H, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 9.4 Hz, AlCH–CH=C*H*), 6.86 (m, 2 x 1 H, Ph–*H*), 6.92 (m, 1 H, Ph–*H*), 6.99 (m, 1 H, Ph–*H*), 7.04–7.12 (m, 4 x 1 H, Ph–*H*), 7.28 (m, 2 x 1 H, Ph–*H*), 7.37 (m, 1 H, Ph–*H*), 7.49 (m, 1 H, Ph–*H*).

^{13}C NMR (125.76 MHz, C_6D_6, 298 K, ppm): δ = 14.28, 15.64, 18.58, 20.40, 22.99, 23.46, 23.75, 24.36, 24.47, 24.72, 24.72, 24.84, 24.84, 24.89, 24.96, 25.00, 25.49, 25.63, 26.31, 26.60, 27.40, 28.22, 29.00, 29.10, 29.84, 32.50, 26.93 (β-*C*H$_3$, *C*H(CH$_3$)$_2$, CH(*C*H$_3$)$_2$, N*C*(*i*Pr), 73.99 (Al–*C*), 100.93 (γ-*C*H), 113.08, 118.25, 121.76, 123.88, 124.19, 124.21, 124.52, 124.56, 125.22, 127.05, 127.70, 128.00, 128.10, 128.20, 130.33, 132.06, 134.52, 136.42, 137.18, 141.52, 141.95, 143.21, 143.58, 145.54, 146.09, 146.79, 149.47, 153.54 (Ph–*C*, *C*H=*C*H–*C*(*i*Pr)=*C*), 170.21 (*C*N).

Correct elemental analysis. Attempts to recrystallize the yellow crystalline material of **25** by dissolving it in a hot toluene/*n*-hexane mixture resulted in the formation of colorless solution which was kept at 4 ºC for crystallization. Colorless rectangular crystals were obtained and were found by spectroscopic and X-ray crystallographic evidence to be **26**.

4.5. Handing and Disposal of Solvents and Residual Waste

1. The recovered solvents were distilled or condensed into cold-traps under vacuum, collected in halogen-free or halogen-containing solvent containers, and stored for disposal.
2. Used NMR solvents were classified into halogen-free or halogen-containing solvents and were disposed as heavy metal wastes and halogen-containing wastes, respectively.
3. The heavy metal residues were dissolved in nitric acid and after neutralization stored in the container for heavy metal wastes.
4. Drying agents such as KOH, $CaCl_2$, $MgCl_2$, $MgSO_4$, and P_4O_{10} were hydrolyzed and disposed as acid or base wastes.
5. Wherever possible, sodium metal used for drying solvents was collected for recycling. The non-reusable sodium metal was carefully treated with cold ethanol and potassium in cold isopropanol and collected into the base-bath cleaning glassware.
6. Ethanol and acetone used for cooling baths were subsequently used for cleaning glassware.
7. The acid bath for cleaning glassware was neutralized with Na_2CO_3 and the resulting NaCl solution was washed off in the water drainage system.
8. The residual of the base both for cleaning glassware was poured into the container for base wastes.

Amount of various types of disposable wastes generated during the work.

Metal containing wastes	5 L
Halogen-containing wastes	4 L
Halogen-free solvent wastes	40 L
Acid wastes	12 L
Base wastes	12 L

4.6. Crystal Data and Refinement Details

Compounds	**1**·0.5 n-hexane	**2**
Formula	$C_{33}H_{57}AlN_3$	$C_{30}H_{49}AlFN_3$
Fw	522.80	497.70
temp (K)	203(2)	200(2)
crystal syst	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*
a (Å)	12.285(3)	13.323(6)
b (Å)	20.125(4)	12.480(2)
c (Å)	14.274(3)	17.979(5)
α (deg)		
β (deg)	110.47(3)	92.57(5)
γ (deg)		
V (Å^3)	3306(1)	2987(2)
Z	4	4
ρ_c (Mg/m^3)	1.050	1.107
μ (mm^{-1})	0.085	0.096
F(000)	1156	1088
θ range (deg)	3.52–25.00	3.61–25.04
Index ranges	$-14 \le h \le 14$	$-15 \le h \le 15$
	$-23 \le k \le 23$	$-10 \le k \le 14$
	$-16 \le l \le 16$	$-16 \le l \le 21$
no. of reflns collected	11566	5643
no. of indep reflns (R_{int})	5786 (0.0346)	5249 (0.1332)
no. of data/restraints/params	5786 / 0 / 350	5249 / 0 / 327
GoF/F^2	1.004	1.069
$R1^a$, $wR2^b$ ($I > 2\sigma(I)$)	0.0418, 0.0994	0.0486, 0.1282
$R1^a$, $wR2^b$ (all data)	0.0586, 0.1101	0.0532, 0.1340
largest diff peak/hole (e·Å^{-3})	0.200 / –0.228	0.519 / –0.300

Compounds	**4**·2 toluene	**7**
Formula	$C_{68}H_{96}AlN_4Se_2$	$C_{29}H_{41}AlClIN_2$
Fw	1181.37	606.97
temp (K)	133(2)	133(2)
crystal syst	monoclinic	monoclinic
space group	*C*2	*P*2(1)/*n*
a (Å)	19.104(4)	12.594(1)
b (Å)	17.561(4)	19.493(1)
c (Å)	12.286(3)	13.502(1)
α (deg)		
β (deg)	129.10(3)	116.47(1)
γ (deg)		
V (Å^3)	3199(1)	2967(1)
Z	2	4
ρ_c (Mg/m^3)	1.227	1.359
μ (mm^{-1})	1.225	1.218
F(000)	1252	1248
θ range (deg)	1.80–24.81	1.84–24.86
Index ranges	$-22 \le h \le 22$	$-14 \le h \le 14$
	$-20 \le k \le 20$	$-22 \le k \le 22$
	$-14 \le l \le 13$	$-15 \le l \le 15$
no. of reflns collected	18430	28829
no. of indep reflns (R_{int})	5488 (0.0718)	5005 (0.0343)
no. of data/restraints/params	5488 / 1 / 312	5005 / 0 / 317
GoF/F^2	0.996	1.092
$R1^a$, $wR2^b$ ($I > 2\sigma(I)$)	0.0433, 0.1112	0.0322, 0.0939
$R1^a$, $wR2^b$ (all data)	0.0529, 0.1164	0.0368, 0.0959
largest diff peak/hole (e·Å^{-3})	0.694 / –0.514	0.853 / –0.935

Compounds	**8**·*n*-hexane	**10**
Formula	$C_{64}H_{98}Al_2Cl_2N_2O_2$	$C_{58}H_{82}Al_2N_4O_2$
Fw	1080.32	921.24
temp (K)	133(2)	100(2)
crystal syst	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*n*
a (Å)	13.567(2)	13.652(3)
b (Å)	13.263(2)	13.717(3)
c (Å)	17.359(5)	14.166(3)
α (deg)		
β (deg)	103.76(2)	106.89(3)
γ (deg)		
V (Å^3)	3034(1)	2538(1)
Z	2	2
ρ_c (Mg/m^3)	1.183	1.205
μ (mm^{-1})	0.182	0.867
F(000)	1172	1000
θ range (deg)	1.55–25.40	0.99–58.95
Index ranges	$-16 \le h \le 16$	$-14 \le h \le 15$
	$-15 \le k \le 15$	$-14 \le k \le 14$
	$-20 \le l \le 20$	$-15 \le l \le 15$
no. of reflns collected	46371	14090
no. of indep reflns (R_{int})	5559 (0.0802)	3617 (0.0295)
no. of data/restraints/params	5559 / 0 / 376	3617 / 141 / 337
GoF/F^2	0.923	1.049
*R*1[a], *wR*2[b] ($I > 2\sigma(I)$)	0.0338, 0.0729	0.0328, 0.0851
*R*1[a], *wR*2[b] (all data)	0.0556, 0.0782	0.0364, 0.878
largest diff peak/hole (e·Å^{-3})	0.229 / –0.190	0.330 / –0.257

Compounds	**12**·0.12 toluene·0.05 *n*-hexane	**13**
Formula	$C_{54.14}H_{67.65}AlN_3$	$C_{58}H_{82}Al_2N_4O_2$
Fw	787.44	921.24
temp (K)	100(2)	100(2)
crystal syst	monoclinic	monoclinic
space group	*C*2/*c*	*P*2/*c*
a (Å)	21.560(4)	22.605(4)
b (Å)	10.457(2)	12.583(2)
c (Å)	48.816(8)	19.132(3)
α (deg)		
β (deg)	97.26(3)	102.68(2)
γ (deg)		
V (Å^3)	9128(3)	5310(2)
Z	8	4
ρ_c (Mg/m^3)	1.146	1.153
μ (mm^{-1})	0.670	0.829
F(000)	3412	2000
θ range (deg)	2.18–59.07	3.51–58.97
Index ranges	$-23 \le h \le 23$	$-23 \le h \le 24$
	$-11 \le k \le 11$	$-13 \le k \le 13$
	$-45 \le l \le 43$	$-21 \le l \le 20$
no. of reflns collected	30396	28366
no. of indep reflns (R_{int})	6498 (0.0374)	7554 (0.0360)
no. of data/restraints/params	6498 / 126 / 624	7554 / 97 / 654
GoF/F^2	1.023	1.025
$R1^a$, $wR2^b$ ($I > 2\sigma(I)$)	0.0369, 0.0859	0.0344, 0.0850
$R1^a$, $wR2^b$ (all data)	0.0463, 0.0910	0.0421, 0.0895
largest diff peak/hole (e·Å^{-3})	0.200 / –0.265	0.213 / –0.240

Compounds	**14**	**16**
Formula	$C_{40}H_{61}AlN_4$	$C_{55}H_{61}AlN_4$
Fw	624.91	805.06
temp (K)	133(2)	203(2)
crystal syst	monoclinic	orthorombic
space group	*P*2(1)/*c*	*P*2(1)2(1)2(1)
a (Å)	10.161(2)	12.285(2)
b (Å)	17.380(4)	12.981(2)
c (Å)	22.274(5)	30.001(6)
α (deg)		
β (deg)	101.89(3)	
γ (deg)		
V (Å^3)	3849.1(13)	4784.4(16)
Z	4	4
ρ_c (Mg/m^3)	1.078	1.118
μ (mm^{-1})	0.084	0.082
F(000)	1386	1728
θ range (deg)	1.87-24.71	3.55-25.01
Index ranges	$-11 \le h \le 11$	$0 \le h \le 14$
	$-20 \le k \le 20$	$-1 \le k \le 15$
	$-26 \le l \le 24$	$-35 \le l \le 35$
no. of reflns collected	33356	4675
no. of indep reflns (R_{int})	6560 (0.1511)	4658 (0.0188)
no. of data/restraints/params	6560/0/424	4658/0/555
GoF/F^2	0.911	1.096
$R1^a$, $wR2^b$ ($I > 2\sigma(I)$)	0.0541, 0.0974	0.0614, 0.1530
$R1^a$, $wR2^b$ (all data)	0.1198, 0.1096	0.0848, 0.1740
largest diff peak/hole (e·Å^{-3})	0.313/-0.271	0.271/-0.282

Compounds	**17**	**18**
Formula	$C_{41}H_{51}AlN_4$	$C_{31}H_{43}AlN_2$
Fw	626.84	470.65
temp (K)	133(2)	133(2)
crystal syst	triclinic	monoclinic
space group	*P*-1	*P*2(1)/*n*
a (Å)	11.704(3)	12.199(1)
b (Å)	12.612(2)	16.932(1)
c (Å)	12.980(4)	13.974(1)
α (deg)	86.460(2)	
β (deg)	77.11(2)	103.87(1)
γ (deg)	86.40(2)	
V (Å^3)	1861.7(7)	2802(1)
Z	2	4
ρ_c (Mg/m^3)	1.118	1.116
μ (mm^{-1})	0.087	0.093
F(000)	676	1024
θ range (deg)	1.61-24.88	1.92–24.83
Index ranges	$-13 \le h \le 13$	$-14 \le h \le 14$
	$-14 \le k \le 14$	$-19 \le k \le 19$
	$-15 \le l \le 15$	$-16 \le l \le 16$
no. of reflns collected	27600	29105
no. of indep reflns (R_{int})	6396 (0.0536)	4818 (0.0486)
no. of data/restraints/params	6396/0/424	4818 / 0 / 325
GoF/F^2	1.015	1.030
$R1^a$, $wR2^b$ ($I > 2\sigma(I)$)	0.0391, 0.0915	0.0349, 0.0867
$R1^a$, $wR2^b$ (all data)	0.0539, 0.0979	0.0502, 0.0916
largest diff peak/hole (e·Å^{-3})	0.210/-0.235	0.263 / –0.255

Compounds	**19**	**20**·0.5 *n*-hexane
Formula	$C_{33}H_{45}AlN_2$	$C_{54}H_{64}AlN_2$
Fw	496.69	768.05
temp (K)	133(2)	133(2)
crystal syst	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*
a (Å)	18.844(4)	14.641(3)
b (Å)	8.732(2)	19.674(4)
c (Å)	20.080(4)	16.162(3)
α (deg)		
β (deg)	112.61(1)	99.78(3)
γ (deg)		
V (Å^3)	3050(1)	4588(2)
Z	4	4
ρ_c (Mg/m^3)	1.082	1.112
μ (mm^{-1})	0.089	0.081
F(000)	1080	1660
θ range (deg)	1.89–24.82	1.65–24.81
Index ranges	$-22 \le h \le 22$	$-17 \le h \le 17$
	$-10 \le k \le 10$	$-23 \le k \le 23$
	$-21 \le l \le 23$	$-19 \le l \le 19$
no. of reflns collected	14555	49895
no. of indep reflns (R_{int})	5145 (0.0394)	7919 (0.0648)
no. of data/restraints/params	5145 / 141 / 476	7919 / 0 / 524
GoF/F^2	0.968	0.986
$R1$[a], $wR2$[b] ($I > 2\sigma(I)$)	0.0364, 0.0820	0.0430, 0.1020
$R1$[a], $wR2$[b] (all data)	0.0582, 0.0877	0.0671, 0.1100
largest diff peak/hole (e·Å^{-3})	0.163 / –0.208	0.170 / –0.204

Compounds	**21**	**22**
Formula	$C_{58}H_{75}AlN_5$	$C_{44}H_{51}AlN_2O_2$
Fw	869.21	666.85
temp (K)	133(2)	133(2)
crystal syst	monoclinic	triclinic
space group	*P*2(1)/*c*	*P*-1
a (Å)	22.289(5)	10.232(5)
b (Å)	13.057(3)	11.111(4)
c (Å)	18.765(4)	18.195(7)
α (deg)		89.49(1)
β (deg)	109.71(3)	87.96(1)
γ (deg)		63.51(1)
V (Å^3)	5141(2)	1850(1)
Z	4	2
ρ_c (Mg/m^3)	1.123	1.197
μ (mm^{-1})	0.081	0.774
F(000)	1884	716
θ range (deg)	1.84–24.87	2.43–58.83
Index ranges	$-26 \le h \le 26$	$-11 \le h \le 11$
	$-15 \le k \le 15$	$-11 \le k \le 12$
	$-22 \le l \le 19$	$0 \le l \le 20$
no. of reflns collected	53490	5023
no. of indep reflns (R_{int})	8850 (0.0825)	5023 (0.0000)
no. of data/restraints/params	8850 / 0 / 602	5023 / 0 / 443
GoF/F^2	0.958	1.053
*R*1[a], *wR*2[b] ($I > 2\sigma(I)$)	0.0560, 0.1371	0.0864, 0.2678
*R*1[a], *wR*2[b] (all data)	0.0933, 0.1508	0.0888, 0.2694
largest diff peak/hole (e·Å^{-3})	0.589 / –0.437	1.19 / –0.675

Compounds	**23**·0.89ether·0.11toluene	**24**·0.45ether·0.55 toluene
Formula	$C_{42}H_{69}AlN_2O_3Si_2$	$C_{72.73}H_{108.85}Al_2N_4O_{0.43}S_2Si_2$
Fw	733.15	1220.28
temp (K)	100(2)	100(2)
crystal syst	triclinic	monoclinic
space group	*P*-1	*Cc*
a (Å)	10.166(2)	18.903(1)
b (Å)	12.783(3)	18.624(1)
c (Å)	17.392(4)	20.125(1)
α (deg)	77.18(3)	
β (deg)	87.82(3)	94.36(1)
γ (deg)	81.05(3)	
V (Å^3)	2177(1)	7065(1)
Z	2	4
ρ_c (Mg/m^3)	1.118	1.147
μ (mm^{-1})	0.139	1.571
F(000)	800	2650
θ range (deg)	0.76–23.61	3.34–60.32
Index ranges	$-10 \le h \le 10$	$-20 \le h \le 20$
	$-11 \le k \le 13$	$-20 \le k \le 20$
	$-16 \le l \le 19$	$-22 \le l \le 22$
no. of reflns collected	8590	15565
no. of indep reflns (R_{int})	4994 (0.0192)	9399 (0.0347)
no. of data/restraints/params	4994 / 0 / 451	9399 / 2 / 772
GoF/F^2	1.025	1.022
$R1$[a], $wR2$[b] ($I > 2\sigma(I)$)	0.0488, 0.1232	0.0351, 0.0779
$R1$[a], $wR2$[b] (all data)	0.0511, 0.1253	0.0433, 0.0813
largest diff peak/hole (e·Å^{-3})	0.478 / –0.470	0.342 / –0.187

Compounds	**25**	**26**
Formula	$C_{59}H_{78}AlN_3$	$C_{59}H_{78}AlN_3$
Fw	856.22	856.22
temp (K)	133(2)	133(2)
crystal syst	monoclinic	triclinic
space group	*P*2(1)/*n*	*P*-1
a (Å)	12.350(1)	11.806(8)
b (Å)	26.264(2)	12.766(5)
c (Å)	16.011(1)	19.718(8)
α (deg)		76.04(3)
β (deg)	104.05(1)	74.54(4)
γ (deg)		64.63(4)
V (Å^3)	5038(1)	2560(2)
Z	4	2
ρ_c (Mg/m^3)	1.129	1.111
μ (mm^{-1})	0.081	0.079
F(000)	1864	932
θ range (deg)	1.52–24.81	1.08–24.81
Index ranges	$-14 \le h \le 14$	$-13 \le h \le 13$
	$-30 \le k \le 31$	$-15 \le k \le 15$
	$-18 \le l \le 15$	$-22 \le l \le 23$
no. of reflns collected	24428	39096
no. of indep reflns (R_{int})	8626 (0.0929)	8758 (0.0409)
no. of data/restraints/params	8626 / 0 / 586	8758 / 0 / 270
GoF/F^2	1.011	1.039
*R*1[a], *wR*2[b] ($I > 2\sigma(I)$)	0.0633, 0.1360	0.0595, 0.1415
*R*1[a], *wR*2[b] (all data)	0.1059, 0.1551	0.0751, 0.1496
largest diff peak/hole (e·Å^{-3})	0.433 / –0.251	0.644 / –0.527

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6. Abbreviations

Ar	aryl, aromatic group
av	average
B.p.	boiling point
*t*Bu	tertiary butyl
Calcd	calculated
d	day(s)
d	density
dec	decompose
deg	degree
η	hapto
EI	electron impact ionization
Et	ethyl
IR	infared
J	coupling constant
K	Kelvin
L	β-diketiminato groups (ligands)
NMR	nuclear magnetic resonance
m/e	mass/charge
Me	methyl
min	minute(s)
M.p.	melting point
MS	mass spectrum
Ph	phenyl
ppm	parts per million
*i*Pr	isopropyl
R	organic groups
THF	tetrahydrofuran
μ	bridging
V	volume
v	wave number
Z	number of molecules in the unit cell

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